THE COMPARATIVE REACTIVITIES OF CHLORINE ATOMS ON CHLOROBENZENE AND SOME SUBSTITUTED CHLOROBENZENES, IN A SIMPLE REACTION WITH SODIUM VAPOUR.

By

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C O N T E N T S.

I N T R O D U C T I O N.

The postulation by Kekulé in 1865 of a cyclic structure for the benzene ring must be regarded as one of the most important events in the history of chemistry. On the basis of this postulate, which has of course been amply confirmed by its success in the interpretation of experimental findings, chemists have been able to study an extraordinarily large number of compounds, and reduce their studies to an orderly system, while the analogous postulates of cyclic structures for pyridine, thiophene, pyrrole, etc. have done like service.

Yet, while the structures of many substances of great complexity have been elucidated on the assumption of a cyclic structure for benzene and similar compounds, there remain outstanding a number of problems relating even to some of the simplest types of benzene compounds. One of such problems is the question of benzene substitution and the replacement of substituents in benzene - the question of the origin and nature of the "directive effect" of substituents in the benzene nucleus; and the closely related question of the influence of such substituents on the other atoms or groups attached to the nucleus. Towards the solution

of this question the present essay is a contribution.

The study of substituted benzene rings was first put on a sound basis by the well-known work of Körner in 1874, when he showed how the positions of the different substituents might be determined. Since that time a very great amount of work has been done on the ease of substitution in different benzene compounds, the relative ease of substitution in different positions, and the relative ease of replacement of different substituents in different positions. Thus Holleman in 1915, at the commencement of his systematic study of replacement of substituents in benzene compounds, found that no less than five hundred and seventy-four papers had been published dealing with the problem. He adds "Après l'étude soignée de ces 574 mémoires, on arrive au résultat vraiment désolant qu'ils sont presque sans valeur pour une étude plus détaillée du problème ici posé." It may be estimated that since 1915 the number of papers on the same subject will have been approximately doubled; and this is one reason for omitting any detailed discussion of the literature of the subject. Another reason is that as in Holleman's case, few if any of the papers published are directly relevant to the present study, since the experiments on which they are based were performed under conditions very different from the

present investigation, as will appear later.

Along with the immense number of papers dealing chiefly with experimental investigations of the problem, there have appeared at times papers of predominantly theoretical interest, which have sought to propound theories which should serve to explain the experimental findings. The forms of such theories have altered with time, as our general knowledge of the structure of molecules has altered and improved, and have gained greater completeness as experimental technique has improved. It may be of interest to outline briefly two such theories of recent development - the one, with which is associated the names of Lapworth, Robinson and Ingold, having been developed more or less empirically from the experimental findings of organic chemistry, and the other, due to E. Hückel, having been deduced from quantum-mechanical considerations of the benzene ring.

The Lapworth-Robinson-Ingold Theory.

This theory may be regarded as being based ultimately on the resultsof experiments on the orientating effect of ionised substituents in the benzene ring. Such substituents thus consist of a free electric pole attached to the ring. It is found that such poles, if positive, have a strong meta-directing effect, while if negative they direct to the

ortho- and para-positions. It is plausible to attribute the directing effects of such substituents to their electric charge.

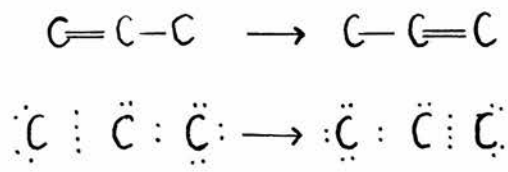
This idea is then easily extended to groups containing polar linkings, such as the nitro-group $-N\begin{matrix}^{+}\\ \diagdown\\ \diagup\end{matrix}\begin{matrix}O\\ \bar{O}\end{matrix}$ and the sulphone group $-S\begin{matrix}^{++}\\ \diagdown\\ \diagup\end{matrix}\begin{matrix}\bar{O}\\ \bar{O}\end{matrix}$, both of which are m-directing.

It has been shown experimentally ((1), p. 800), and the result is confirmed by measurements of the electric moments of the molecules, that certain substituents introduced into the benzene ring produce a displacement of the electrons to or from the substituent, depending presumably on the tendency of the atom of the substituent attached to the ring, to complete its octet of electrons, compared with the same tendency of carbon atoms.

All the above substituents thus produce a shift of the electrons of the ring. This effect will be shown as a distortion of the normal symmetry of the charge about the carbon atom to which the substituent is attached. This distortion will, in turn, alter the charge-distribution about the adjacent carbon atoms, and so on, so that the disturbance is relayed round the ring. This effect is called the inductive effect.

A second effect may occur when the atom attached to the carbon atom of the ring possesses one or more unshared electrons. This effect consists of an actual

or incipient movement of an electron, while remaining in one octet, into or out of another. By analogy with the tautomeric displacement of double bonds, (which is a well-known example of the effect) thus:-



this effect is called the tautomeric effect.

There exists also a third effect, called the "direct effect", which consists of the direct action through space of the electric field of the substituent group, on the atoms of the ring, thus modifying the field round these atoms.

The position at which substitution will occur depends, firstly, on the magnitude and sign of the electric charges produced by these effects, at the different atoms in the ring, and secondly, on whether the substituent group introduced is one which seeks positions of positive or negative charge.

The effect of one substituent on the ease of removal of another will depend similarly on its effect on the charge-distribution in the ring, and the effect of this charge-distribution on the strength of the bond attaching the other to the ring.

This theory is satisfactory in that it can be brought into harmony with most of the experimental findings. On the other hand, the various charge-

distributions assumed are largely empirical assumptions, and quantitative predictions of the results of a reaction cannot be deduced from it.

[Note. The terminology adopted by different writers at different times, in their discussion of the Lapworth-Robindon- Ingold theory, varies considerably. For this reason it may be as well to remark that in the above discussion, the terms used by Ingold in an account of the theory in the Recueil des Travaux Chimiques des Pays-Bas (1) have been adhered to throughout .]

Hückel's Theory.

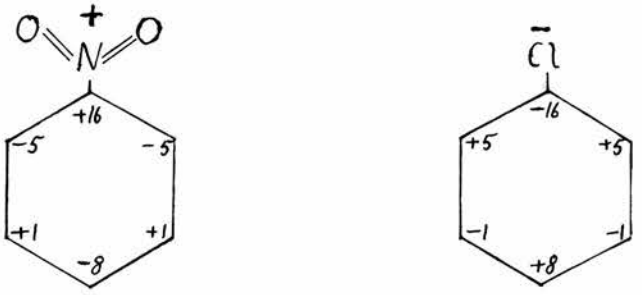
In organic compounds, the carbon-carbon, carbon-hydrogen, and other bonds are in general homopolar, that is, they arise from the pairing of two electrons, one coming from each atom joined by the "bond". In most compounds it is found that every valence-electron of all the atoms composing it, is accounted for by its being involved in a bond - indeed this rule has become, through its general fulfilment, one of the tests which decides the acceptability of a proposed structure for a compound. The rule, however, is not fulfilled in the case of "aromatic" compounds such as benzene, unless special assumptions are made. In benzene, for example, each carbon atom gives one elèctron towards each of the two bonds joining it to the adjacent

carbon atom, and one towards the bond joining it to a hydrogen atom - thus accounting for three of its four valence electrons. Various theories have been advanced at different times to dispose of the fourth electron in a bond, none being completely satisfactory, but it is generally considered that the "aromatic" properties of benzene and similar substances, and their derivatives, arise from the electrons thus left over, since the disposition of these electrons in homopolar bonds, e.g. by reduction, destroys the aromatic properties of the ring.

E. Hückel (2) first investigated by quantum-mechanical methods the relative stability of ring systems of the general formula C_nH_n , in which each carbon atom is attached by one bond to each of two adjacent carbon atoms and a hydrogen atom, thus leaving it (as with the carbon atoms in benzene) with one electron to be disposed of. He found that such systems would have a maximum stability if n were equal to 2, 6, 10 ···· etc., for in these cases the undisposed electrons form a closed group somewhat analogous to the outer shells of electrons of the inert gases. Now C_2H_2 is not cyclic, while $C_{10}H_{10}$ has not been found; but the important result emerges that C_6H_6 , benzene, should be (as is well established experimentally) a particularly stable compound. Penney (3) has recently revised these calculations in more detail, considering also the effect of the electrons involved in the bonds

and has arrived at a similar result.

Hückel (4) then extended his calculations to the case of substituted benzenes. The method adopted was to consider the substituent group as causing a disturbance to the normal state of the six electrons not involved in bonds, and then to calculate the distribution of the charge in the ring due to these six electrons. The results obtained are represented by the following diagrams,



in which the figures opposite each carbon atom of the ring indicate the sign and density of the charges at these atoms due to the six electrons not involved in bonds. The figures are in arbitrary units.

The alternation of the sign of the charge on going round the ring is very significant, and is in accordance with the general findings of organic chemistry; as, for instance, that nitro-benzene in reaction tends to become substituted in the meta-position, while chlorobenzene is more easily attacked in the ortho- and para-positions.

The value of Hückel's results has been questioned by Lapworth and Robinson (5), (6). (See also Hückel

and Hückel (7)). They hold that the results of the theory are in conflict with experimental results, which would lead one to the conclusion of an alternation of electric charge similar in form but opposite in sign to that given by the theory. The matter may be considered to be in abeyance at the moment, but the results of the theory in its present form are not acceptable to organic chemists.

The general conclusion from the theories discussed is that considerable progress has been made towards the representation of the experimental results by a theory which attempts to explain the results found by an alternation in the value of an electric charge at different carbon atoms in the ring; it is probable that the origin of this charge is, in part at least, the presence of electrons not involved in homopolar bonds.

The basis of the Lapworth-Robinson-Ingold theory consists entirely of experiments done in solution on the reactions of benzene and its substituents, and only in a few cases has the effect of disturbing factors due to the solvent, or to possible complex-formation in the solution, been considered, although it is known that such factors may have an important influence. Thus, for example, the bromination of phenol proceeds quite differently in water (8) from the same bromination in certain organic solvents (9).

Further, the mechanism of substitution reactions has sometimes been held (e.g., by Holleman (10)) to involve primarily the formation of an addition compound, with subsequent rearrangements. Again, Brewin and Turner (11) adduce evidence for the supposition that in the substitution by ethoxy or amino groups of chlorine in nitro-chlorobenzenes, a complex is first formed by the addition of the reagent to the nitro-group.

Any such effects as these must involve radical alterations of the charge distribution in the benzene ring, compared with the normal charge distribution. The construction of a theory to account for all the experimental facts would therefore appear to be an affair of the greatest difficulty, and it would be a matter of some importance if a few investigations could be carried out in such a way as to rule out of consideration the disturbances enumerated above.

Now the possibility of such disturbances is scarcely to be avoided in experiments in the liquid phase; on the other hand, it would be difficult to carry out the majority of organic reactions in the gas phase, which is pre-eminently suitable for the investigation of reactions in their simplest forms.

The development, however, by von Hartel and Polanyi (12) of a method for determining the rates of reaction of sodium vapour with the vapours of some organic halogen compounds, appeared to offer the

possibility of studying some very simple reactions of benzene derivatives. The present essay is a description of experiments performed in this connection.

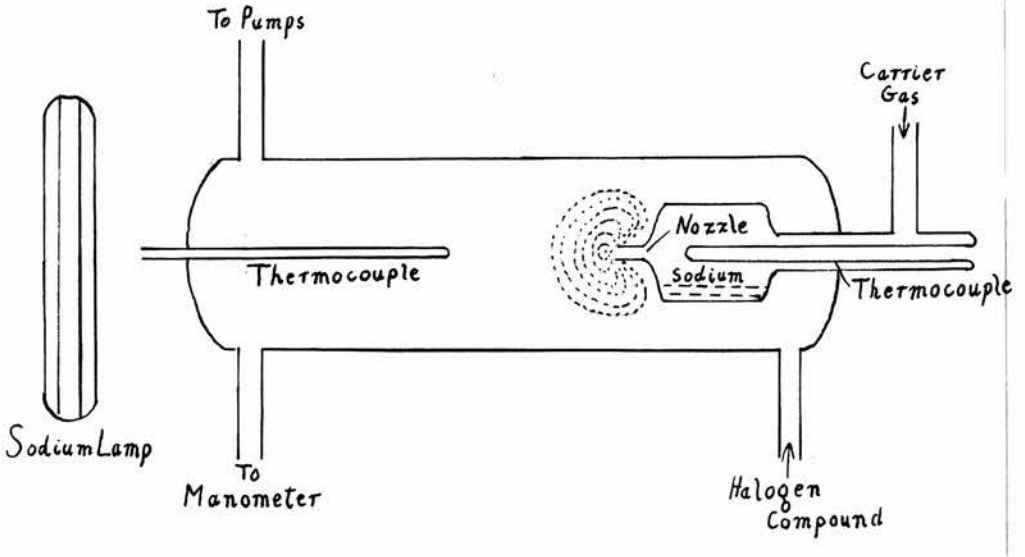
DESCRIPTION Of The METHOD Of EXPERIMENT.

The experiments are concerned with the measurement of the velocity constants of reactions of the type

$$Na + Ar \cdot Cl = NaCl + Ar$$

(where Ar represents an aromatic nucleus) and the method followed is a slightly altered form of that of Polanyi and von Hartel (12) as modified by von Hartel, Meer and Polanyi (13).

Sodium vapour is blown by means of a carrier gas through a nozzle into a chamber containing the vapour of the halogen compound, the speed of its reaction with which is to be measured. The rate of entry of the sodium vapour into the chamber is so adjusted that the vapour spreads out in the chamber in a spherical zone (not a long tongue), while the speed of flow of the carrier gas through the nozzle must be high enough to prevent appreciable diffusion of the carrier gas back into the nozzle. The sodium vapour in the reaction chamber is made to emit light by resonance excitation with a sodium lamp outside the chamber, and is thus rendered visible.



The reaction tube is heated electrically by external windings.

It can readily be seen that this will afford a means of finding the rate of the reaction of the sodium vapour with the halogen compound, for if all the other factors are kept constant, then a large zone of sodium vapour will be evidence of a slower reaction than a small one.

A mathematical development of a formula for the numerical evaluation of the velocity constant of the reaction was given by von Hartel and Polanyi (12), and is as follows:-

In the stationary state the partial pressure x of sodium vapour at a radius r, from the centre of the nozzle, will depend on the rate of diffusion of the vapour outwards from the nozzle, and on the rate of consumption of the sodium vapour by the reaction. The equation is

$$\frac{d^2x}{d\tau^2} + \frac{2}{\tau}\cdot\frac{dx}{d\tau} - \frac{K.p_{He}.x}{\delta} = 0 \qquad (Equ^n\ 1)$$

where x is the partial pressure of sodium vapour in a shell of radius r,

K is the velocity constant of the reaction defined by

$$-\frac{dx}{dt} = K \cdot p_{Hal} \cdot x \qquad (Equ^n\ 2)$$

p_{Hl} is the partial pressure of the vapour of the halogen compound in the shell,

δ is the diffusion coefficient of sodium vapour in the gases in the reaction chamber.

It is assumed by the authors that the partial pressure p_{Hl} of the halogen compound is constant throughout the reaction chamber, for since the halogen compound is present in the reactions investigated, in great excess over the sodium vapour, its concentration will be only negligibly altered by the reaction.

A solution of the above equation is

$$x = \frac{A}{r} \cdot e^{-r\sqrt{\frac{K \cdot p_{Hal}}{\delta}}} \qquad (Equ^n\ 3)$$

where A is an integration constant.

To eliminate A, and give K in absolute terms, the limiting conditions must be determined. For these we may plausibly assume that

(1) When $r = r_o$, the radius of the nozzle, the partial pressure of the sodium vapour is the same as before it had left the nozzle, i.e., if

it can be taken that the carrier gas is completely saturated with sodium vapour, the partial pressure of sodium vapour at $r = r_0$ is the vapour pressure p_{Na} of sodium at the temperature of the tube. Thus we write for $r = r_0$, $x = p_{Na}$.

(2) At the circumference of the visible zone (say $r = R_0$) the partial pressure of sodium vapour will be p_0 , the lowest pressure which can be detected. This may be determined by another experiment. Thus we write for $r = R$, $x = p_0$.

Inserting these two limiting conditions, we obtain

$$p_{Na} = \frac{A}{r_0} \cdot e^{-r_0\sqrt{\frac{K \cdot p_{H\ell}}{\delta}}} \qquad (Equ^n\ 4)$$

$$p_0 = \frac{A}{R} \cdot e^{-R\sqrt{\frac{K \cdot p_{H\ell}}{\delta}}} \qquad (Equ^n\ 5)$$

Dividing the first of these equations by the second, we eliminate A, obtaining

$$\frac{p_{Na}}{p_0} = \frac{R}{r_0} \cdot e^{(R-r_0)\sqrt{\frac{K \cdot p_{H\ell}}{\delta}}}$$

whence we may easily derive

$$K = \frac{\left(\log_e \frac{p_{Na}}{p_0} - \log_e \frac{R}{r_0}\right)^2}{(R - r_0)^2} \cdot \frac{\delta}{p_{H\ell}} \qquad (Equ^n\ 6)$$

the required expression for the velocity constant.

Another expression for this constant is given by the authors, derived as follows:-

Neglect the term $\frac{2}{r}\frac{dx}{dr}$ in equation (1). This term is due to the fact that we are considering diffusion outwards through a spherical zone - it takes care of the increase in area of a shell of the sphere as the radius of the shell increases.

The equation thus becomes

$$\frac{d^2x}{dr^2} - \frac{K.\rho_{He}}{\delta}.x = 0 \qquad (Equ^n\ 7)$$

a solution of which is

$$x = A.e^{-r.\sqrt{\frac{K.\rho_{He}}{\delta}}}$$

Proceeding as before, and inserting the limiting conditions, $x = p_{Na}$ at $r = 0$, $x = p_0$ at $r = R$, we obtain eventually

$$K = \frac{\left(\log_e \frac{p_{Na}}{p_0}\right)^2}{R^2}.\frac{\delta}{\rho_{He}} \qquad (Equ^n\ 8)$$

It will be noticed that this equation does not involve r_0, nor the assumption that there exists a small zone of radius r_0 in which the partial pressure of sodium vapour is constant and equal to p_{Na}.

von Hartel and Polanyi found that the two equations (6) and (8) gave in practice values for K which did not differ considerably, and they used equation (8) for the evaluation of their experiments.

It became evident in the course of the work

to be described that the mathematical treatment described above was not satisfactory for the evaluation of the present experiments, and required modifications which will be described in due course.

However, from equation (6) may be decided what experimental observations will be required to evaluate the velocity constant of the reaction. These are as follows:-

P_{Na} - the vapour pressure of sodium. (This involves the assumption that the carrier gas is completely saturated with sodium vapour. von Hartel and Polanyi (loc. cit.) declared that they had satisfied themselves that this assumption was justified, and as in the present work the rates of flow of carrier gas were of the order of one-tenth of the rates employed by them, the validity of the assumption was accepted without further investigation). The vapour pressure of sodium is most easily determined from its temperature, and careful determinations of the vapour pressure of sodium at different temperatures which have been made at different times (14), (15), (16), (17), (18).

P_{Hl} - the partial pressure of the halogen compound in the reaction chamber. This pressure cannot be determined directly, as besides the halogen compound there are present in the

reaction chamber sodium vapour and the carrier gas. By determining, however, the total pressure in the chamber (p_T), and the rates of flow into the chamber of the carrier gas and the halogen compound, f_c and f_{Hl} respectively, we may obtain p_{Hl} from the equation

$$p_{Hl} = \frac{f_{Hl}}{f_c + f_{Hl}} \cdot p_T$$

since the partial pressure of sodium vapour is relatively negligible.

δ - the diffusion coefficient of sodium vapour in the gases in the reaction chamber. von Hartel and Polanyi (12) state that they had determined by special experiments the diffusion coefficient of sodium vapour in hydrogen and nitrogen, which were the carrier gases used by them. These values thus obtained they used in the majority of experiments performed by them, in which they considered that the disturbing effect of the halogen compound on this coefficient might be neglected. In other experiments where the partial pressure of the halogen compound became appreciable, they corrected the values obtained for the carrier gas according to simple considerations deduced from the kinetic theory of gases. In a later paper, von Hartel, Meer and Polanyi (13) found

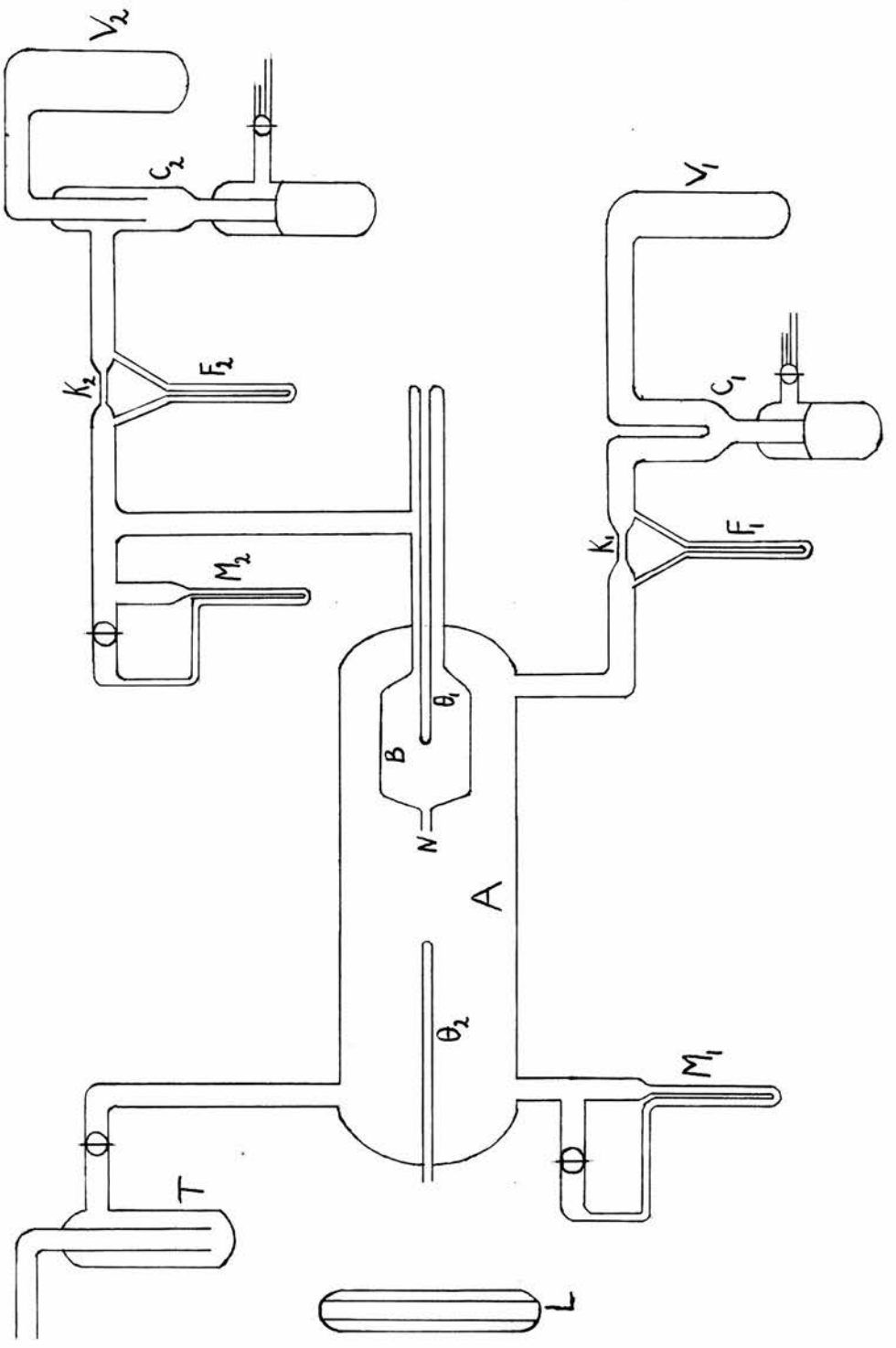
that the admixture of even small proportions of the vapours of organic compounds to hydrogen or nitrogen altered considerably the diffusion coefficient of sodium vapour in these gases, and a series of experiments was carried out to determine this effect.

In the present experiments, it was decided to use xylene vapour as the carrier gas, in order to simplify the determination of the diffusion coefficient. von Hartel, Meer, and Polanyi, in their experiments on the diffusion coefficient of sodium vapour, used mixtures of pentane and hydrogen, or pentane and nitrogen, of known composition. Pentane was used as being a representative substitute, not reacting with sodium, for the aliphatic halogen compounds they investigated, and they assumed that the diffusion coefficient of sodium vapour in a certain mixture of say pentane and hydrogen, would not differ much from the diffusion coefficient in a mixture of an aliphatic halogen compound and hydrogen. In the present work it was assumed that the diffusion coefficient of sodium vapour in xylene vapour would not differ much from its diffusion coefficient in a mixture of xylene vapour with the vapour of the (aromatic) halogen compounds

employed. In connection with the modified mathematical treatment mentioned above, it will become evident that unless some such direct assumption can be made, the experiments would admit of evaluation of the velocity constant only with the greatest difficulty. Special experiments were therefore performed to determine the diffusion coefficient of sodium vapour in xylene vapour.

p_0 - the minimum detectable partial pressure of sodium vapour. This was determined by an appropriate experiment.

To allow of the determination of all the necessary quantities, the apparatus was arranged as shown in the following diagrammatic sketch.


V2
C2
K2
F2
M2
V1
C1
K1
F1
B
θ1
N
A
θ2
M1
T
L

Key to Letters.

A - The reaction chamber which was of Pyrex glass, 5 cm. in bore.

B - The sodium vessel.

N - The nozzle through which the sodium vapour was blown into the chamber. Its bore was 2 mm.

θ_1 - A tube permitting the insertion of a thermo-couple for determining the temperature of the sodium.

θ_2 - A similar tube approaching to within 5 cm. of the nozzle N, to permit the use of a thermo-couple to determine the temperature in the reaction chamber.

M_1 - A differential sulphuric acid manometer for determining the total pressure in the reaction chamber.

V_1 - A vessel containing the halogen compound.

C_1 - A simple mercury cut-off.

F_1 - A flowmeter for measuring the rate of flow of the halogen compound; it consisted of two limbs of a mercury manometer separated by a capillary K_1.

M_2 - A differential sulphuric acid manometer, associated with the carrier gas flowmeter.

F_2 - A flowmeter for measuring the rate of flow of the carrier gas. It consisted of two limbs of a sulphuric acid manometer, separated by a capillary K_2.

C_2 - A simple mercury cut-off.

V_2 - A vessel containing liquid xylene.

T - A liquid air (or carbon-dioxide-snow ether) trap.

L - The sodium lamp.

Since organic compounds of low vapour pressure were the subject of study, the various pressure gauges could not be McLeod gauges, as the vapours would have condensed in the bulb on compression. Mercury manometers were not sufficiently sensitive, in general, while oil manometers were ruled out by the consideration that the oil would absorb the compounds used. Hence sulphuric acid manometers were used in the places shown.

It was found that a sufficient rate of flow was obtained by using a cooled trap in conjunction with a small mercury vapour pump backed by a Hyvac.

The circulating system adopted by Polanyi and co-workers was not employed, as having no advantage over the system shown.

The rates of flow of the vapours of the compounds were controlled by controlling the temperature of the compounds in the vessels V_1 , V_2.

Some of the organic vapours had a tendency, on standing, to condense on and dissolve tap-grease, and mercury cut-offs were therefore employed where it was advisable.

The sodium lamp used was supplied by The General Electric Company, Ltd. It operated by means of an electric discharge in the manner of a number of different types now advertised. The discharge took place through a tube which was surrounded by another, the space between being evacuated. The lamp gave a powerful light, consisting principally of the sodium D-line with a few much weaker lines of shorter wavelength. The D-line was only slightly "inverted", and the lamp was found quite suitable for exciting sodium resonance radiation, though rather cumbrous to mount.

Certain modifications were made to details of the apparatus as sketched, according as they were necessitated by the different compounds studied. These will be mentioned when dealing with compounds involved.

SUBSTANCES Used In The EXPERIMENTS.

Sodium. The sodium used in the experiments was a commercial variety obtained electrolytically, which was kept under xylol when not in use. It was introduced into the apparatus used in the different experiments, in the form of a thread expressed from a simple sodium press. Its contact with ordinary air was hindered as much as was possible without taking elaborate precautions. When at any time it was necessary to admit air into apparatus containing sodium, the air was passed slowly through a calcium chloride tube and a low temperature trap.

Xylene. "B.D.H. Meta-Xylene" was fractionated and the liquid which distilled between 135°C and 140·5°C was taken. This liquid was refluxed over sodium for an hour and then fractionally distilled off sodium. The fraction distilling between 136·5°C and 139·5°C was taken and was kept over sodium.

No attempt was made to exclude any of the three xylenes, since the main desiderata for the carrier gas were that it should have a molecular structure similar to that of the halogen compounds investigated, and that it should not react with sodium. All the three xylenes were therefore equally suitable for the purpose. The xylene used

in all the experiments was treated as above at the same time - about 200 c.c. were prepared - so that the same substance, even though of indeterminate composition, was used throughout the work.

Sulphuric acid. The sulphuric acid used for titration in the diffusion experiments was prepared from the commercial "pure" acid by dilution with distilled Water.

The acid used in the manometers was B.D.H. "A.R." sulphuric acid. It was transferred into the manometers as quickly as possible and the access of ordinary moist air hindered until the apparatus was completed and evacuated. When it was necessary to admit air to apparatus fitted with sulphuric acid manometers the air was passed slowly through a calcium chloride tube and a cooled trap, except in the case of the diffusion coefficient experiments in which a special tap was used to cut off the manometer when air was admitted.

Apparatus fitted with sulphuric acid manometers was left evacuated overnight before use, in order that the acid might give up dissolved gas.

Mercury. The mercury used in the apparatus was taken from the department stock and washed twice with dilute nitric acid. It was preserved from contact with metals.

Chlorobenzene. The chlorobenzene used was a B.D.H. product which was well washed with sodium carbonate solution, dried and carefully fractionated, the portion distilling at 129·2°C being taken.

Para-chloro-toluene. Para-chloro-toluene was prepared in the routine manner from diazotised para-toluidine by treatment with cuprous chloride, and steam distillation. The product was washed with caustic soda solution, with water, and then repeatedly with sodium carbonate solution, after which it was fractionated, the portion distilling at 159°C to 160°C being taken.

Para-nitro-chlorobenzene. The para-nitro-chlorobenzene was a B.D.H. product which was found to melt fairly sharply, and it was not further purified except for its being distilled into the apparatus in vacuo, the first and last portions being rejected.

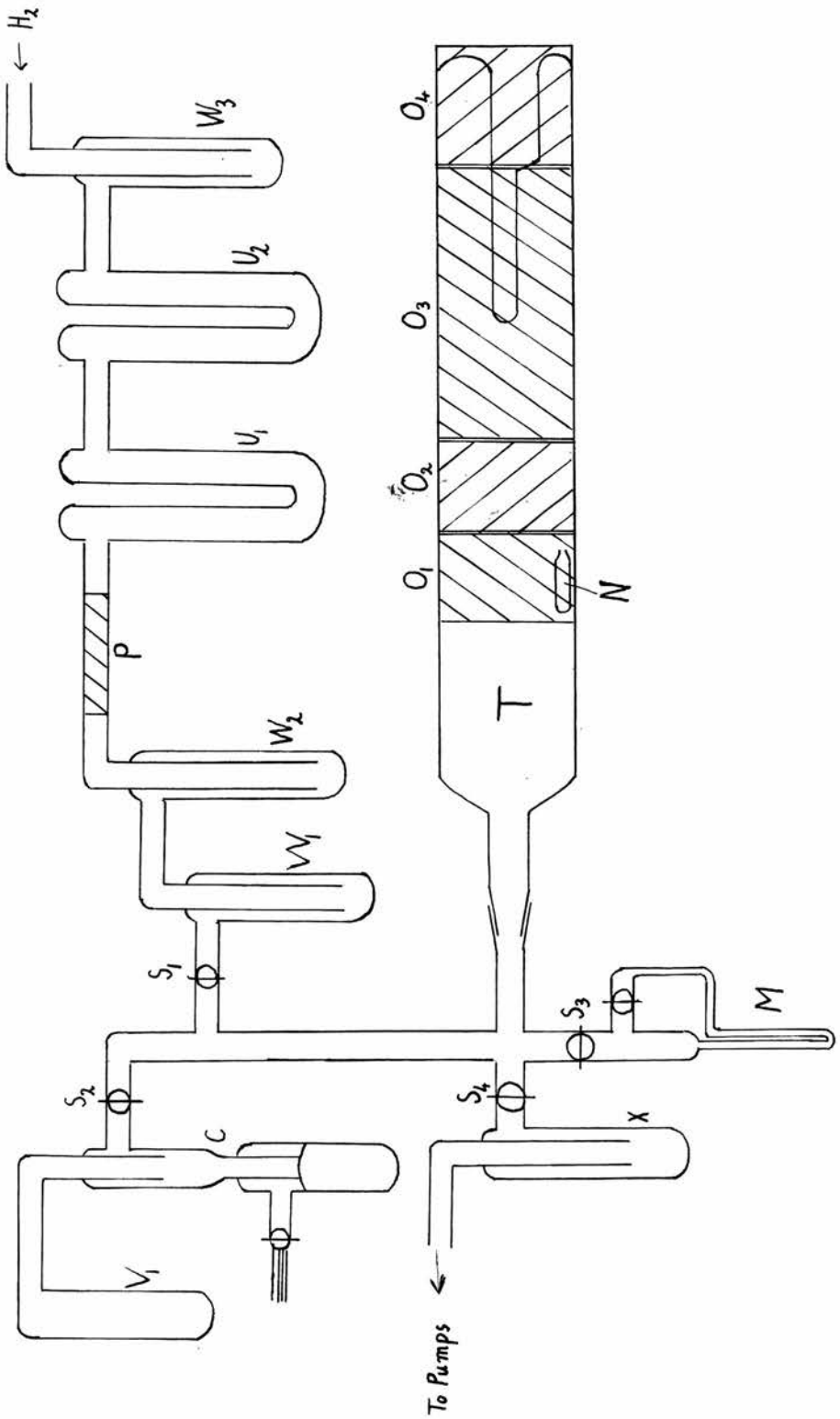
DESCRIPTION Of The PRELIMINARY EXPERIMENTS.

Since, as has been noted, it is necessary, in order to calculate the velocity constant of a reaction investigated by the method described, to know the diffusion coefficient of sodium vapour in xylene vapour, the minimum detectable partial pressure of sodium vapour in the reaction chamber, and the rates of flow of the carrier gas and the halogen compound, preliminary experiments were performed to determine these quantities, and will be described here.

1. The Diffusion Coefficient of Sodium Vapour in Xylene Vapour.

The literature dealing with experiments on diffusion coefficients in general, and on the inter-diffusion of two gases, is by no means extensive, and the diffusion coefficient of sodium vapour in xylene vapour does not appear to have been previously determined. Further, the theory of diffusion is not sufficiently advanced to enable the calculation of such a quantity to be performed, and therefore the experiments here described were undertaken. The diffusion coefficient of sodium vapour in hydrogen, determined by von Hartel, Meer and Polanyi (13), was first found as a check on the experimental technique.

The method and apparatus were similar to those used by von Hartel, Meer and Polanyi (13) in their diffusion coefficient experiments referred to on page 19. The method consists in the distillation in the stationary state of sodium from a known temperature through a tube at a (known) slightly higher temperature, after which it was condensed at room temperature. A diagrammatic sketch of the apparatus is given.


H₂
W₃
U₂
U₁
P
W₂
V₁
S₁
S₂
C
V₁
To Pumps
S₄
S₃
M
X
T
O₁
O₂
O₃
O₄
N

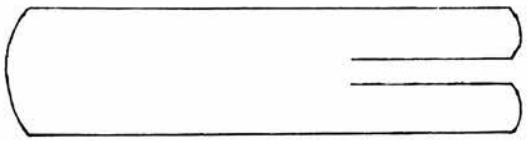
Key to Letters.

T - The tube in which the diffusion took place. It was of Pyrex glass, about five feet in length and two to three cm. in internal diameter. One end was fitted with a ground glass joint to connect it to the remainder of the apparatus (which was of soda-glass) and the other was fitted with a re-entrant tube which permitted two thermometers to be inserted, one extending well into the section covered by the oven O_3, the other to the end of the section covered by oven O_4. The thermometers used in the experiments were carefully standardised with standard thermometers.

O_1, O_2, O_3, O_4 - Electric ovens. O_1 and O_2 were about 15 cm. long and were wound on copper formers which were arranged to surround the tube closely, but sufficiently loosely to permit of their being moved along the tube at will. O_3 was about 40 cm. long and was wound on copper foil wrapped tightly round the tube, so that it was not movable; the copper foil was used to ensure even heating of the section of the tube covered by this oven, up to its extremities.

O_4, like O_1 and O_2 , was wound on a copper former to permit of its being removed from the tube. It was about 20 cm. long and extended a few cm. beyond the end of the tube.

N - A vessel containing sodium. This was provided with a re-entrant exit, thus



in order to avoid spurting of liquid sodium from it when hot.

M - A sulphuric acid manometer.

S_3 - A stop-cock to cut off the manometer M when air was admitted to the tube.

X - A liquid air trap.

S_1 - A stop-cock for admitting hydrogen.

W_1, W_2 - Wash-bottles containing concentrated sulphuric acid .

P - A section of tubing containing palladinised asbestos, through which the hydrogen had to pass.

U_1, U_2 - Soda-lime tubes, containing as usual calcium chloride at the exit ends.

W_3 - A wash-bottle containing nitric acid.

S_2 - A stop-cock for admitting xylene.

C - A simple mercury cut-off, to prevent xylene vapour from standing in contact with the grease on the stop-cocks.

V_1 - Vessel containing liquid xylene.

S_4 - A stopcock to isolate the apparatus from the pumps.

The hydrogen used in the experiments was prepared from A.R. zinc and hydrochloric acid in a Kipp generator, and purified before admission into the apparatus by its being passed through concentrated nitric acid, soda-lime, palladinised asbestos heated to 200°C, and concentrated sulphuric acid.

The xylene was de-gassed before use by repeated freezing and evacuating.

At the commencement of the experiment, after the erection of the apparatus - including the insertion of the sodium vessel N - the tube was thoroughly evacuated through the liquid air trap by a mercury vapour pump backed by a Hyvac oil-pump. The tube was meanwhile heated to about 380°C for about an hour. The oven O_4 was then removed from the tube, and the part of the tube heated by it was cooled by an air-blast,

so that sodium was distilled from the vessel N to that part of the tube for about three hours, when ovens O_2 and O_3 were regulated to about 365°C, and oven O_1 was switched off and moved away along the tube. The apparatus was then flooded twice with hydrogen or xylene vapour (according as the experiment in question was to determine the diffusion coefficient of sodium vapour in hydrogen or xylene vapour), and finally pumped out to a suitable pressure (about 1 millimetre), the stopcock S_4 being then closed. The oven O_4 was now replaced on the tube and regulated to a temperature of about 353°C. After a vew minutes had elasped, in order that the stationary state might be attained, oven O_2 was switched off, moved along the tube, and the section of tube previously heated by it was rapidly cooled by an air-blast. At this moment the real experiment began, and the time was noted. After the passage of a suitable time, the experiment was stopped by removing oven O_4 and cooling the end of the tube by an air-blast, the time being again noted. Oven O_3 was then switched off.

When the tube had cooled, air was admitted to the apparatus, the tube was cut, and the sodium which had condensed in the experiment was removed by being washed out with water. This aqueous sodium solution was then titrated against a standard solution of sulphuric acid, methyl orange being used as indicator, to determine the amount of sodium present.

The diffusion coefficient of sodium vapour in the gas used in the experiment could now be calculated, using a formula derived from Fick's first law of diffusion. This formula is (19)

$$D = \frac{M.l}{c_g.q.t.\left(\log_e \frac{c_g}{c_g - c_s}\right)}$$

where

D is the diffusion coefficient of sodium vapour;

M is the quantity in mols of sodium diffusing during the experiment;

l is the distance diffused by the sodium vapour;

q is the cross-section of the tube T;

t is the time of diffusion;

c_q is the total concentration of gas in the tube;

c_s is the saturation concentration of the sodium vapour in the tube heated by oven O_4.

If we express the concentrations as pressures, this becomes for the diffusion coefficient at 760 mm. pressure

$$D = \frac{M.l.R.T.}{760.q.t.\left(\log_e \frac{1}{1 - \frac{P_{Na}.T}{P_g.T_{Na}}}\right)}$$

where

R is the gas constant;

T is the temperature of the tube;

T_{Na} is the temperature of the part of the tube heated by oven O_4 ;

p_{Na} is the vapour pressure of sodium at temperature T_{Na}, calculated from T_{Na} and Ladenburg and Thiele's equation (16).

$$\log (p_{Na} \cdot T_{Na}^{1.178}) = 11.413 - \frac{26249}{4.573} \cdot \frac{1}{T_{Na}}$$

p_g is the total pressure in the tube.

A selection of results obtained for the diffusion coefficient of sodium vapour in hydrogen and in xylene vapour are tabulated below.

TABLE.

Diffusion Coefficient of Sodium Vapour in Hydrogen.

Mols Sodium Diffused $=M$	Length Diffused $=l$	Temperature of Tube $=T$	Cross-Section of Tube $=q$	Time of Diffusion $=t$	Temp of Sodium $=T_{Na}$	Vapour Pressure of Sodium $=p_{Na}$	Total Pressure in Tube $=p_g$	Diffusion Coefficient $=D$
	cm.	°K	$cm.^2$	secs.	°K	mm.	mm.	
$20 \cdot 55 \times 10^{-4}$	38·5	638·8	5·94	6000	625	0·0859	2·46	3·20
$16 \cdot 55 \times 10^{-4}$	39·0	639	4·15	2400	625	0·0859	0·825	3·02
$24 \cdot 30 \times 10^{-4}$	38·1	639	4·15	1800	626	0·0889	0·465	2·99

Mean value of D = 3·07 at 639°K and 760 mm.

The value obtained by von Hartel, Meer and Polanyi (13) for the diffusion coefficient of sodium vapour in hydrogen was 3·14 at 655°K and 760 mm. The average value obtained thus agrees very well with their value, and the agreement is even further improved if the temperature variation of the diffusion coefficient is taken into account.

In these experiments with hydrogen a McLeod gauge was employed instead of the sulphuric acid manometer.

TABLE.

Diffusion Coefficient of Sodium Vapour in Xylene Vapour.

Mols Sodium Diffused $= M$	Length Diffused $= l$	Temperature of Tube $= T$	Cross-Section of Tube $= q$	Time of Diffusion $= t$	Temperature of Sodium $= T_{Na}$	Vapour Pressure of Sodium $= P_{Na}$	Total Pressure in Tube $= P_g$	Diffusion Coefficient $= D$
	cm.	°K	$cm.^2$	secs.	°K	mm.	mm.	
$4·32\times10^{-4}$	38·5	639	3·94	10800	627	0·0918	1·76	0·376
$4·82\times10^{-4}$	39·5	633	4·34	9000	625	0·0859	1·32	0·370
$5·74\times10^{-4}$	38·7	639	4·71	9000	618	0·0687	0·947	0·352

Before calculating the mean value of D, it is to be noted that in the second row of the table, the experiment took place at 633°K instead of at 639°K, as in the other experiments. The value of D entered must therefore in this case be multiplied by the factor $(639/633)^{1·5}$. The new value of D obtained is 0·375. Now we find

Mean value of D = 0·368 at 639°K and 760 mm.

The experimental error to which these determinations are liable is probably about five per cent.

It was found that the glassware subjected to the action of hot sodium vapour in these experiments deteriorated rapidly. Ordinary soda-glass became unworkable after about two experiments and was therefore not used. Pyrex glass gradually altered in its properties and after about four experiments became difficult to work. A more serious fault with Pyrex glass was, however, the fact that it gradually assumed on the surfaces reached by hot sodium vapour a coating of some brown substance. This coating was more or less soluble in water, which tended to upset both the value of the quantity of sodium titrated, and the ease of determination of the end-point of the titration. The coating might be largely removed before each experiment by standing in contact with water or hydrochloric acid. The proneness to ~~such~~ attack by the sodium increased, however, with each experiment, and for this reason it was found advisable to replace the tube after each two experiments.

On page 25 it has been noted that the "xylene" used was probably a mixture of the three isomeric xylenes, with the meta-compound predominant. For this reason the above determination of the diffusion

coefficient may not have quite the significance of a determination for a perfectly pure compound. On the other hand, there would appear, on physical grounds, no reason to expect any considerable difference between the diffusion coefficients of sodium vapour in the vapours of any of the three xylenes, so that until a more rigorous determination is made the value found in these experiments may be accepted as approximately the value of the diffusion coefficient of sodium vapour in the vapour of any of the three xylenes.

2. The Minimum Detectable Partial Pressure of Sodium Vapour.

This was determined after the apparatus had been set up according to the sketch on page 21.

A current of xylene vapour was allowed to flow over the sodium while the reaction chamber was slowly heated electrically. The temperature of the sodium chamber, when first the issuing vapour was observed as it left the nozzle, was noted.

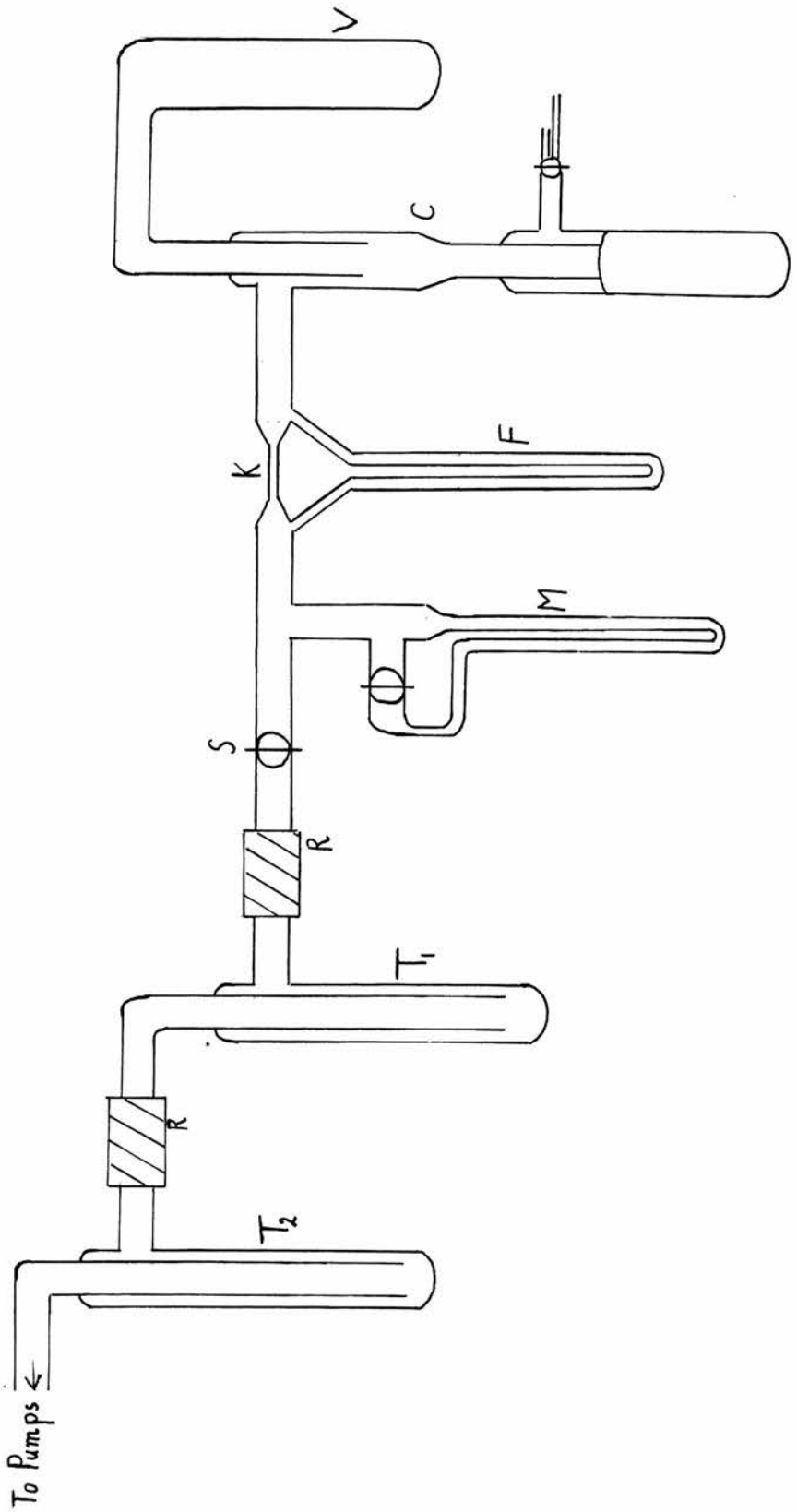
This was done on two separate occasions; the temperatures found were 163°C and 163°C. The vapour pressure of sodium at this temperature is according to Ladenburg and Thiele's equation (16) $1{\cdot}38 \times 10^{-5}$ millimetres, and according to Edmondson and Egerton's equation (15) $1{\cdot}41 \times 10^{-5}$ millimetres.

In view of the fact that the eye is probably

less able to detect the minimum partial pressure at the edge of a zone of higher sodium vapour concentration than when presented only with this minimum, it was decided to take as the minimum detectable partial pressure of sodium vapour the figure $1 \cdot 5 \times 10^{-5}$ millimetres.

3. Calibration of the Xylene Vapour Flowmeter.

This flowmeter F, with its associated manometer, was connected up in the manner sketched on the following page.


V
C
F
K
M
S
R
T1
R
T2
To Pumps

Key to Letters.

V - A vessel containing xylene.

C - A mercury cut-off.

F - The Flowmeter, consisting of a differential sulphuric acid manometer, between the arms of which was joined a piece of capillary tubing K of length 10·2 cm. and diameter 1·93 millimetres.

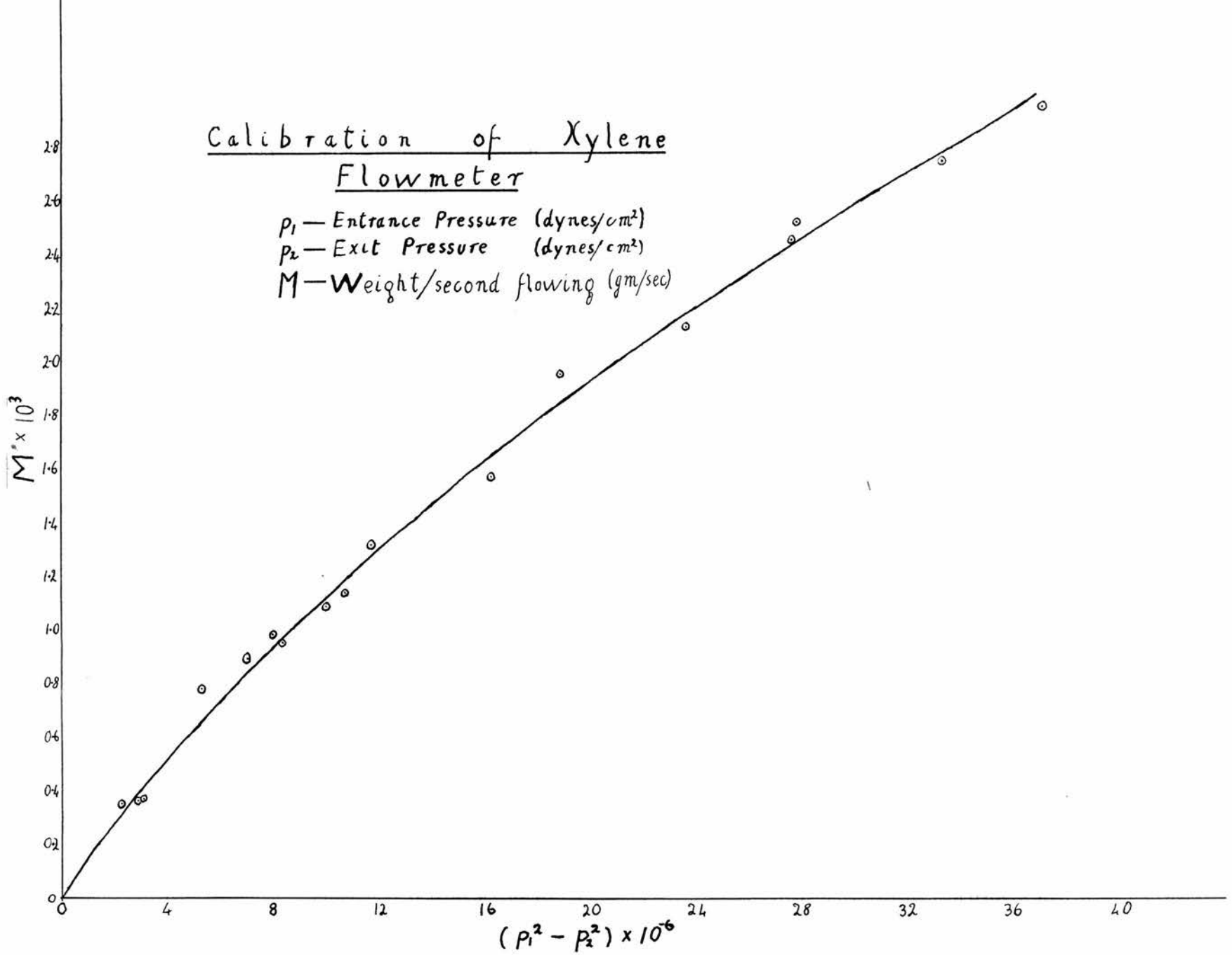
M - The sulphuric acid manometer associated with the flowmeter.

S - A stop-cock.

T_1 , T_2 - Two liquid air traps connected, as shown, by short pieces of heavy-walled rubber tubing R.

The apparatus, after erection, was pumped out and the xylene de-gassed by repeated freezing and evacuation, the trap T_2 being meanwhile surrounded with liquid air.

For each experiment the trap T_1 was removed and weighed. After it had been replaced, the pumps were started and trap T_2 immersed in liquid air. The stopcock S was opened and the zero readings of the manometer and flowmeter were noted. By operating the cut-off, xylene vapour was allowed to flow through the


Calibration of Xylene Flowmeter
P_1 — Entrance Pressure (dynes/cm²)
P_2 — Exit Pressure (dynes/cm²)
M — Weight/second flowing (gm/sec)
M × 10³
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
0
4
8
12
16
20
24
28
32
36
40
$(P_1^2 - P_2^2) \times 10^{-6}$

apparatus; after a moment or two, to allow the stationary state to be attained, the weighed trap T_1 was also surrounded with liquid air. This marked the commencement of the experiment, and the time was noted. The readings of the flowmeter and manometer were observed, and after a sufficient amount of xylene had been received into the trap T_1 (one to three grams), the flow of xylene vapour was cut off, the stopcock closed, and the time again taken. The trap T_1 was now removed for weighing. Access of water vapour from the air, which would have condensed in it while it was still cold, was prevented by closing the tubes from it. When it had attained room temperature it was weighed.

This was repeated several times, the rate of flow being varied by warming or cooling the xylene reservoir, and the results obtained were plotted on the graph attached, in which the weight of xylene transferred per second is plotted against the difference between the squares of the pressures at the two ends of the flowmeter capillary.

It was found that the line which best fitted the points obtained is

$$p_1^2 - p_2^2 = 6{\cdot}9 \times 10^9 M + 1{\cdot}82 \times 10^{12} M^2$$

where

p_1 is the pressure at the "high pressure" end of the capillary, measured in dynes/cm.^{2};

p_2 is the pressure at the "low pressure" end of the capillary, measured in dynes/cm.^{2} ;

M is the weight, in grams, of xylene vapour transpiring per second.

Brillouin's formula (20) for the viscous flow of a gas is

$$p_1^2 - p_2^2 = \frac{p}{\rho}\left[\frac{16.\eta.l.M.}{\pi.r^4\left(1+\frac{4\xi}{r}\right)} + \frac{2M^2}{\pi^2 r^4}\right]$$

where

p_1 , p_2 , M are as above.

p is "normal pressure" (760 mm. of mercury) in dynes/cm.^{2} ;

ρ is the density of the gas at normal temperature and pressure;

η is the viscosity coefficient.

l is the length of the capillary;

r is the radius of the capillary;

ξ is the "slip coefficient", equal approximately to the mean free path of the gas molecules.

It was found that the value of the viscosity coefficient calculated from Brillouin's equation was not constant, the deviation being systematic.

Nevertheless, the similarity in form of Brillouin's equation and the empirical experimental

equation is suggestive. A large part of the deviation from constancy of the viscosity coefficient must arise from the difference in the coefficient of M^2 in the equations, that required by Brillouin's equation being $0{\cdot}50 \times 10^{12}$, while that found was $1{\cdot}82 \times 10^{12}$.

If the whole discrepancy is put down to this difference, we may identify the coefficients of M in the two equations and so find a value for , the viscosity coefficient of xylene vapour, thus

$$\frac{P}{\rho} \times \frac{16\eta l}{\pi r^4} = 6{\cdot}9 \times 10^9$$

(neglecting the correction for slip). The value for η obtained from this equation is η = 55 micropoises.

There do not appear to have been made any reliable determinations of the viscosity coefficient of xylene vapour. An interesting paper by Lowry and Nasini (21), however, suggests that in certain series of similar compounds, the replacement of a hydrogen atom by a methyl group causes a fairly regular change in some of the physical properties, such as the vapour viscosity and Sutherland constant of the compounds. If we may assume that this holds also for the replacement of a second hydrogen atom by a methyl group, it appears from a consideration of their results that a probable value for the viscosity coefficient of xylene at 20°C would be 64 micropoises.

There is thus a measure of agreement between the two results - an agreement which would be increased

slightly if the correction for slip were applied to the present determination. In view, however, of the assumptions made in arriving at these values, it can only be said that on the whole a value of about 60 micropoises is probable for the viscosity coefficient of xylene vapour at 20°C.

The reason for the deviations from Brillouin's equation is not clear. As the subject is only incidental to the present work, it was not pursued further.

In the reaction velocity experiments, the graph was used directly for relating the experimental observations to the rate of flow of xylene vapour.

4. Calibration of Flowmeters for the Halogen Compound Vapours.

The calibrations of these flowmeters were performed in each case immediately before the experiment on the corresponding reaction velocity constants.

The flowmeters for chlorobenzene and para-chlorotoluene were calibrated in situ on the apparatus, as sketched on page 21, by a method similar to that employed in calibrating the flowmeter for xylene vapour. Two further traps T_2 and T_3 were inserted in series between the trap T of the apparatus and the pumps by means of short pieces of heavy-walled rubber tubing.

The trap T_2 was weighed, and the weight of halogen compound condensing in it in a known period of time was found, together with the corresponding pressure difference reading of the flowmeter. The trap T_3 was used during the establishment of the stationary state. The results of the calibration experiments (in which varying rates of flow were obtained by varying the temperature of the halogen compound reservoir) were plotted on graphs.

No attempt was made to calculate viscosity coefficients for these compounds, partly because this lay outwith the scope of the present work, and partly because the flowmeter capillaries were required to be very fine, in order to provide sufficient sensitivity to operate the differential mercury manometers, and it is probable that conditions of turbulent flow prevailed.

The method of calibration in the case of para-nitro-chlorobenzene was altered to take account of the low vapour pressure of this compound at room temperature. The apparatus was modified in the sense of the sketch given on page 83, and a discussion of the alterations is appended to it.

FIRST REACTION VELOCITY EXPERIMENTS.

When the appropriate preliminary experiments described in the last section had been completed, including the calibration of a flowmeter for chlorobenzene, the apparatus described on pages 12 to 24 was put into action to determine the velocity of the reaction between the vapours of sodium and of this compound. Chlorobenzene was one of the substances used by von Hartel and Polanyi (12) in their first work on reactions between sodium vapour and vapours of organic halogen compounds. It was re-investigated, however, as a check on the experimental technique, and because its study appeared to be a natural introduction to a study of substituted chlorobenzenes. (It may be noted here that very few studies of the velocities of reactions of substituted chlorobenzenes have hitherto included chlorobenzene; indeed Hückel (4) in 1931 was able to find none, and since then only one paper including chlorobenzene and substituted chlorobenzenes has been published).

In the present experiments with chlorobenzene, the reservoir for the liquid and the appropriate flowmeter were constructed compactly together, so that both could be surrounded by a beaker of water at a suitable temperature to control the rate of flow of the chlorobenzene vapour into the reaction chamber. It was found that in these experiments a suitable

temperature was very slightly above room temperature, and no difficulty was experienced in maintaining constant conditions for considerable periods of time.

It was also found that the luminous zone of sodium vapour in the reaction chamber first became spherical when the xylene reservoir was immersed in ice and water at a temperature of 0°C. This greatly facilitated the operation of the apparatus.

The first experiments were performed with the reaction chamber at a temperature of about 275°C, the sodium container being about 12°C cooler. After the first six experiments, in a slight alteration to the apparatus, the reaction chamber thermocouple θ_2 stuck in its tube and broke. As, however, these six experiments had shown that with the existing arrangement of heating ovens the reaction chamber was on the average 12°C hotter than the temperature of the sodium reservoir (shown by the thermocouple θ_1), the loss of the thermocouple was not of much importance, and in subsequent experiments it was assumed that the temperature of the reaction chamber was 12°C above that shown by the thermocouple θ_1. At no future time was any alteration made to the heating ovens.

The experimental observations consisted of the following readings:-

(1) the temperature of the reaction chamber as shown by the galvanometer in circuit with the thermocouple θ_1 (until this thermocouple broke);

(2) the temperature of the sodium reservoir as shown by the galvanometer in circuit with the thermocouple θ_1;

(3) the total pressure in the reaction chamber as shown by the manometer M_1;

(4) the diameter of the luminous zone of sodium vapour, which was read off by means of a centimetre rule;

(5) the rate of flow of chlorobenzene vapour which was found from the readings of the appropriate flowmeter;

(6) the rate of flow of xylene vapour, determined by reading the xylene vapour flowmeter and its associated manometer M_2.

In the following table, which represents the results of these first experiments, these readings led directly to

$T^{\circ}K$, the temperature of the reaction chamber;

$T_{Na}{}^{\circ}K$, the temperature of the sodium reservoir;

p_T, the total pressure in the reaction chamber;

R, the radius of the illuminated sodium zone;

f_{Hl}, the rate of flow of chlorobenzene vapour;

f_c, the rate of flow of the carrier gas (xylene vapour).

The other quantities entered in the table were derived from these readings by calculation, according to the following scheme:-

p_{Na}, the vapour pressure of sodium at temperature T_{Na}, was calculated from Edmondson and Egerton's equation (15)

$$\log_{10} p_{Na} = \frac{-5573.2}{T_{Na}} + 9.7255 - .6794 \log_{10} T_{Na}$$

This equation was used as being probably the most accurate in the temperature range here used.

p_{Hl}, the partial pressure of chlorobenzene in the reaction chamber, was derived from the following equation

$$p_{Hl} = \frac{f_{Hl}}{f_c + f_{Hl}} \cdot p_T$$

δ, the diffusion coefficient of sodium vapour in the gases in the reaction chamber at pressure p_T and temperature T°K was calculated from the equation

$$\delta = D \cdot \frac{760}{p_T} \cdot \left(\frac{T}{639}\right)^{1.5}$$

where D represents the diffusion coefficient of sodium vapour in xylene vapour at 760 mm.

and 639°K, which was found in the preliminary experiments (page 37) to be 0·368.

K_α , the velocity constant of the reaction between sodium vapour and chlorobenzene vapour as derived from the equation (see page 15)

$$K_\alpha = \frac{\left(\log_e \frac{P_{Na}}{P_0} - \log_e \frac{R}{r_0}\right)^2}{(R - r_0)^2} \cdot \frac{\delta}{\rho_{He}}$$

K_β, the velocity constant of the same reaction as derived from the equation (see page 16)

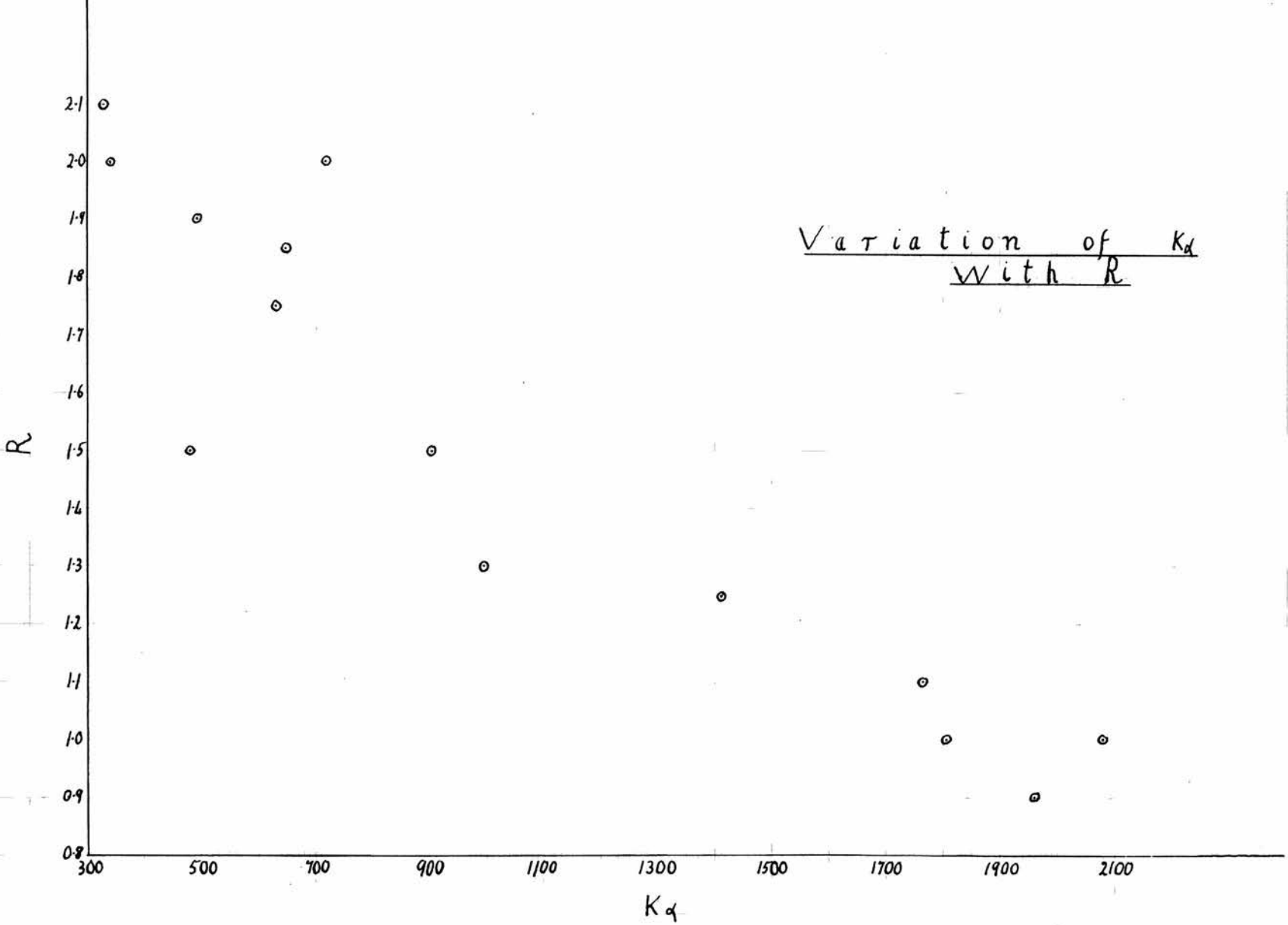
$$K_\beta = \frac{\left(\log_e \frac{P_{Na}}{P_0}\right)^2}{R^2} \cdot \frac{\delta}{\rho_{He}}$$

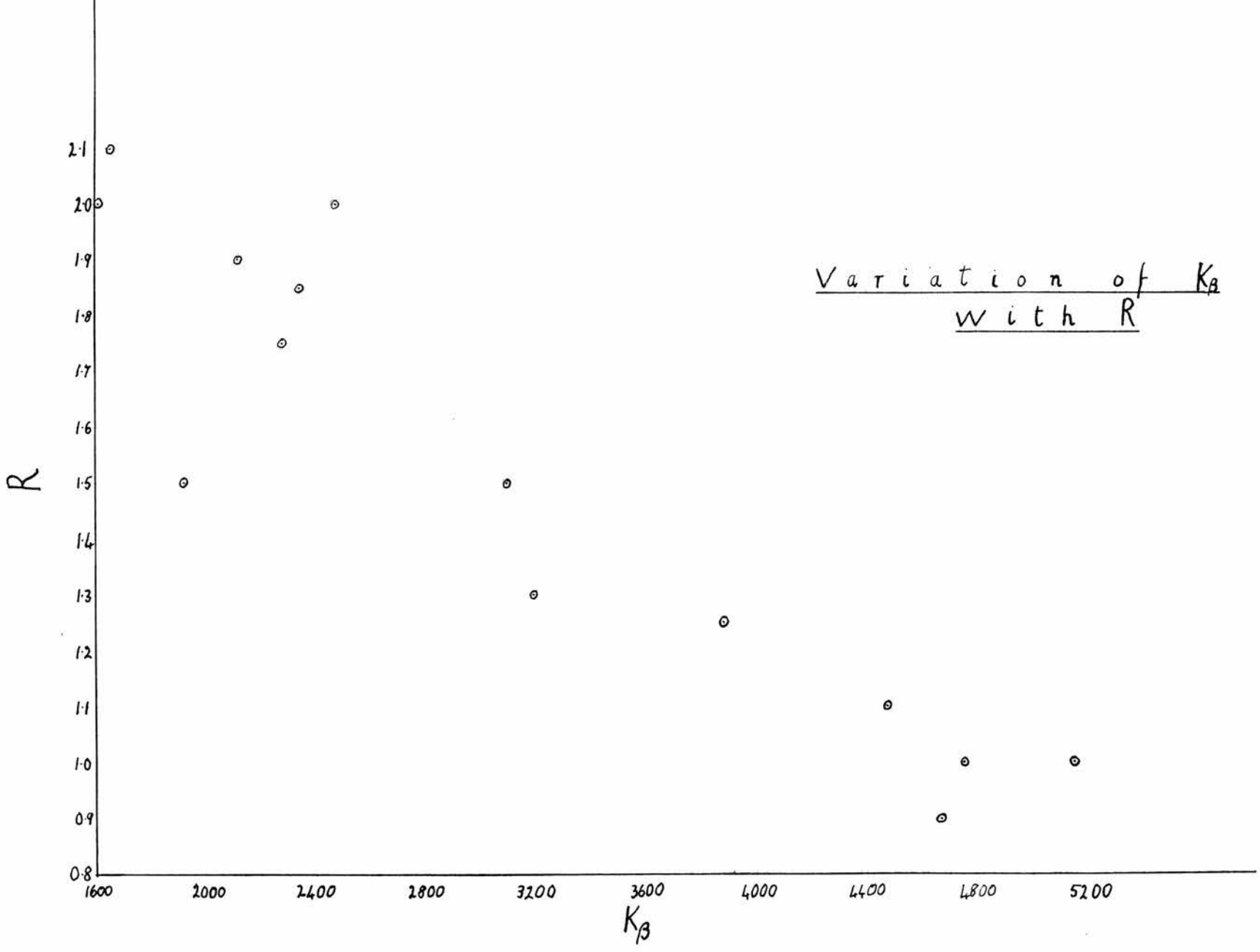
TABLE 1.

Results of Experiments on the Reaction between Sodium Vapour and Chlorobenzene Vapour.

No.	T °K	T_{Na} °K	p_T mm.	R cm.	$f_{Cl} \times 10^8$ mols/sec	$f_{Hl} \times 10^8$ mols/sec	$p_{Na} \times 10^3$ mm	p_{Hl} mm.	δ_l	K_α	K_β
2*	547	536	1·12	2·0	143	470	2·98	0·86	198	336	1610
3*	553·5	540	1·14	1·5	166	490	3·53	0·85	198	901	3090
5*	548	539	1·09	1·9	194	500	3·39	0·785	204	492	2110
6*	547	536	1·09	2·1	193	490	2·98	0·78	203	329	1650
7*	546	533·5	1·39	0·9	65	450	2·67	1·13	159	1960	4670
8*	571	556·5	1·09	2·0	188	600	7·00	0·83	217	718	2470
9	543	531	1·23	1·5	140	900	2·39	1·06	178	479	1920
10	550	538	1·21	1·0	140	850	3·25	1·04	185	2080	5150
11	557	545	1·20	1·25	151	810	4·37	1·01	190	1410	3880
12	545	533	1·21	1·0	164	900	2·62	1·02	182	1800	4760
13	555	543	1·39	1·1	274	580	4·01	0·94	163	1770	4480
20	548	536	1·27	1·3	265	680	2·98	0·91	175	994	3190
25	557	545	1·24	1·75	244	540	4·37	0·85	184	628	2280
26	560	548	1·18	1·85	240	540	4·95	0·82	195	645	2340

The experiments marked with an asterisk in the first column were performed before the thermocouple θ_2 broke.


Variation of K_d With R
R
2·1
2·0
1·9
1·8
1·7
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
300
500
700
900
1100
1300
1500
1700
1900
2100
K_d


Variation of K_β with R
R
2·1
2·0
1·9
1·8
1·7
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
1600
2000
2400
2800
3200
3600
4000
4400
4800
5200
K_β

There are several points to be noted about this table:

1. The two values for the velocity constant represented by K_α and K_β are in no case even approximately equal, but differ by a factor of three very approximately. This is quite at variance with what von Hartel and Polanyi (12) found to be the case in their experiments.

2. The values for the velocity constant represented by K_α and K_β are widely different from the corresponding values found by von Hartel and Polanyi (loc. cit.) for the reaction between sodium vapour and chlorobenzene vapour, which are respectively 17,300 and 17,270.

3. Neither of the quantities K_α or K_β is even approximately constant. A further inspection of the table shows that both these quantities increase as the value of R decreases. This tendency is represented on the accompanying graphs which show further that there exists an approximately reciprocal relation between K_α or K_β, and R.

In view of the difference between the results obtained by von Hartel and Polanyi for chlorobenzene mentioned above, and the present results, an examination of the difference between the experimental

technique in the two cases was undertaken. These differences were found to be:

1. The use of xylene vapour as carrier gas in place of hydrogen or nitrogen.

2. The use of a different sodium lamp and a different method of viewing the zone of sodium vapour, those workers having observed the shadow of the sodium zone against the bright background of the lamp, whereas in the present case the luminous zone of sodium vapour was viewed against a dark background.

3. The experiment reported by von Hartel and Polanyi was performed at 260°C, in place of the 279°C which was the average temperature in the present case.

4. In von Hartel and Polanyi's experiments (12) the radius R of the zone of sodium vapour was always about one centimetre, while the radius r_0 of the nozzle through which the sodium vapour entered the reaction chamber was 0·25 centimetre. In the present experiments, R varied from about one to two centimetres, while the (internal) radius r_0 of the nozzle was one millimetre.

There does not appear to be in any of these

technical differences any ground for expecting such differences in the results of the experiments as are noted on page 54 in connection with Table 1.

The systematic variation of K_α and K_β with R suggested, however, that the mathematical treatment of the experimental observations might be at fault in some particular. Accordingly, closer investigation of the theoretical aspect of the matter was made and is presented in the following section.

MATHEMATICAL DISCUSSION Of The EXPERIMENT.

The main assumptions made by von Hartel and Polanyi (12) in their mathematical treatment of the experiment, which was described briefly on pages 13 to 17, were:

1. That the sodium vapour leaves the nozzle with zero forward velocity as it enters the reaction chamber, and diffuses freely and evenly in all directions through space from a small region at the nozzle; it occupies, therefore, a spherical zone whose centre is approximately at the centre of the end of the nozzle. This assumption simplifies the treatment of the problem of the distribution of the sodium vapour in the reaction chamber, as this distribution is controlled only by simple diffusion conditions and by the reaction which consumes the sodium vapour.
2. That the vapour of the halogen compound is distributed evenly throughout the reaction chamber, and therefore throughout the zone occupied by the sodium vapour. This assumption simplifies the calculation of the part played by the reaction in governing the distribution of the sodium vapour.

The possibility of the existence of an approximately spherical zone of sodium vapour, showing the absence of any appreciable forward velocity of the sodium vapour when it has left the nozzle, may easily be demonstrated experimentally. To this extent, therefore, the first assumption is readily justified.

The question of the existence of a small region at the end of the nozzle, in which the partial pressure of sodium vapour has not yet been diminished either by diffusion from it of the sodium vapour or by consumption of the sodium by the reaction, was considered by von Hartel and Polanyi to be undecided, in particular as regards the size of such a region, this being one reason for their adoption of equation (8) on page 16. The question has been further discussed by Haber and Sachsse (22) in an investigation of the reaction of sodium vapour with oxygen. They conclude that under appropriate experimental conditions such a region must be considered to exist, since in face of the flow of carrier gas from the nozzle little or none of the oxygen (or halogen compound in the present experiments) can be present at the mouth of the nozzle. They show, further, that if the linear velocity of flow of the gases through the nozzle is reasonably large, the amount of oxygen (or halogen compound) diffusing back into the nozzle against this flow can only be small. They noticed a deposit inside the nozzle and ascribed it to sodium oxide; such a deposit was also noticed in the

present experiments, but in view of the temperature of the reaction chamber, it is probable that the deposit is similar to that described on page 38, due to the action of sodium vapour on the hot glass.

In view of these arguments, it seems permissible to conclude that the first assumption may be considered justified, at least to a reasonable approximation.

The second assumption is discussed at some length by von Hartel and Polanyi (loc. cit.). They conclude that provided the reaction is reasonably slow, so that the partial pressure of the vapour of the halogen compound is considerably greater than that of the sodium, the consumption by the reaction of the halogen compound must be negligible, and therefore they conclude that the second assumption is tenable.

It is suggested, however, that the distribution of the vapour of the halogen compound in the reaction chamber cannot be controlled entirely by the consumption of this compound by the reaction, but must also be affected by the presence of the carrier gas. Were the distribution of the carrier gas in the reaction chamber uniform, then of course its presence would have no appreciable effect on the reaction, but this distribution cannot be considered to be uniform.

Since the carrier gas is able to flow into

the reaction chamber, its pressure a moment before leaving the nozzle must be greater than the pressure in the chamber. As it leaves the nozzle its forward velocity will fall to zero in a properly conducted experiment, for if it retained any forward velocity the sodium vapour carried by it must share this velocity, and a non-spherical sodium zone would result.

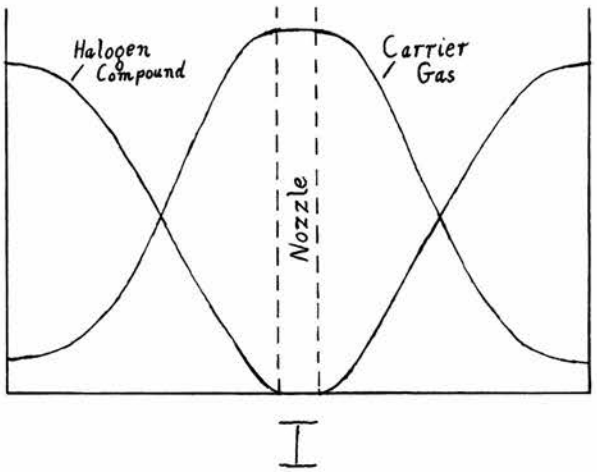
Near the walls of the reaction chamber the partial pressure of the carrier gas will have fallen considerably, since it is being pumped off. Since in a fairly large tube with a relatively small exit, like the reaction chamber, the rate of flow through the wide tube is very low (if it were otherwise, the zone of sodium vapour would be distorted from the shape of a sphere), we may regard the carrier gas as being pumped off nearly equally in all directions away from the nozzle.

Near the walls, therefore, the halogen compound vapour and the carrier gas are the only gases present, and contribute according to their relative proportions to the total pressure in the chamber. At the exit of the nozzle, however, there exists a small zone containing only the carrier gas and a relatively minute pressure of sodium vapour, with none of the vapour of the halogen compound.

Hence, the distribution of the carrier gas, and therefore of the halogen compound vapour, is far from uniform. The partial pressure of the vapour of

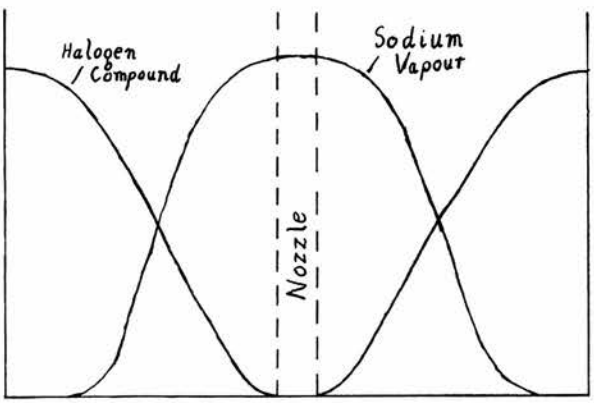
the halogen compound, in fact, is quite large near the walls of the reaction chamber and diminishes practically to zero at the surface of a small zone at the end of the nozzle.

The distribution of these two gases in the reaction chamber will be somewhat as shown in diagram I.



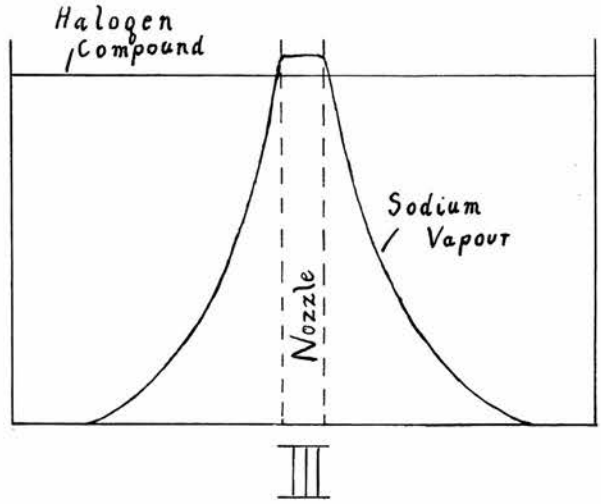
I

The effect of this uneven distribution of the vapour of the halogen compound on the distribution of sodium vapour may be anticipated to be somewhat as sketched in diagram II.



II

For purposes of comparison, the anticipated distribution of sodium vapour in the case of a uniform distribution of the vapour of the halogen compound is sketched in diagram III.



III

In these two diagrams (II and III) the pressure scale is very different for the two substances.

Summarising the differences in the distribution of sodium vapour in the two cases illustrated by diagrams II and III, we may say that in the first case, of non-uniform distribution of halogen compound vapour, the partial pressure of sodium vapour falls off near the nozzle much less rapidly than in the second case.

It now remains to translate these considerations into mathematical terms.

We consider, as before, the partial pressure of sodium vapour to be determined, at any point in the

zone occupied by it, by the diffusion of the vapour from the nozzle, and by the consumption of the vapour by its reaction with the halogen compound. The appropriate equation is

$$\frac{d^2x}{dr^2} + \frac{2}{r}\cdot\frac{dx}{dr} - \frac{K}{\delta_1}\cdot x\cdot y = 0 \qquad (Equ^n\ 1)$$

where

x is the partial pressure of sodium vapour at a point,

r is the distance of that point from the centre of the exit of the nozzle,

y is the partial pressure of the halogen compound at the point,

K is the velocity constant of the reaction between the halogen compound and sodium, in the vapour phase.

K is defined by

$$-\frac{dx}{dt} = K\cdot xy$$

δ_1 is the diffusion coefficient of sodium vapour in the gases in the reaction chamber.

The partial pressure of the vapour of the halogen compound is determined by the diffusion of the vapour from surrounding space towards the nozzle, and by the consumption of the vapour by its reaction with sodium. The equation is

$$\frac{d^2y}{dr^2} + \frac{2}{r}\frac{dy}{dr} - \frac{K}{\delta_2}xy = 0 \qquad (Equ^n\ 2)$$

where

x, y, r, K are as defined for equation(1),

δ_2 is the diffusion coefficient of halogen compound vapour in the gases in the reaction chamber.

Since, however, the partial pressure of the sodium vapour in the experiment is very much less than that of the vapour of the halogen compound, we may neglect the effect of the reaction upon the distribution of the latter vapour. This simplifies equation (2) to give

$$\frac{d^2y}{dr^2} + \frac{2}{r}\cdot\frac{dy}{dr} = 0 \qquad (Equ^n\ 3)$$

Equation (3) has the solution

$$y = a + \frac{b}{r} \qquad (Equ^n\ 4)$$

in which a and b are integration constants, which may be determined by the limiting conditions

$y = 0$ at $r = r_0$

$y = p_{Hl}$ at $r = \infty$

where

r_0 is the radius of the nozzle,

p_{Hl} is the measured partial pressure of the halogen compound vapour.

Equation (4) thus becomes

$$y = p_{He}\left(1 - \frac{r_0}{r}\right) \qquad (Equ^n\ 5)$$

We now substitute the value of y obtained from equation (5) in equation (1), thus

$$\frac{d^2x}{dr^2} + \frac{2}{r}\cdot\frac{dx}{dr} - \frac{Kp_{He}}{\delta_1}x + \frac{Kp_{He}\cdot r_0}{\delta_1}\cdot\frac{x}{r} = 0 \qquad (Equ^n\ 6)$$

In order to obtain a solution of this equation we first make the substitution $x = \frac{u}{r}$ and obtain

$$\frac{d^2u}{dr^2} - \frac{K.\rho_{He}}{\delta_1}.u + \frac{K.\rho_{He}.r_0}{\delta_1}.\frac{u}{r} = 0 \qquad (Equ^n\ 7)$$

Employing a well-known theorem in the theory of differential equations with constant coëfficients, we now suppose u to be the sum of two quantities u_1 and u_2 ($u = u_1 + u_2$) such that

$$\frac{d^2u_1}{dr^2} - \frac{K.\rho_{He}}{\delta_1}.u_1 = 0 \qquad (Equ^n\ 8)$$

$$\frac{d^2u_2}{dr^2} + \frac{K.\rho_{He}.r_0}{\delta_1}.\frac{u_2}{r} = 0 \qquad (Equ^n\ 9)$$

The quantities u_1 , u_2 are obviously completely determined by these two equations, and therefore u is determined.

Now, equation (8) may readily be found to have the solution

$$u_1 = \beta_1.e^{-r\sqrt{\frac{K.\rho_{He}}{\delta_1}}} \qquad (Equ^n\ 10)$$

in which β_1 is an integration constant.

Equation (9) is a particular form of Riccati's equation, which can only be solved in algebraic terms under very restricted conditions. In general, however, it may be solved in terms of Bessel functions. The simplest method of solution in the present case would appear to be the development of a solution in series,

which may than be compared with Bessel function series.

First put

$$\phi = \frac{K.\rho_{He}.r_0}{\delta_1} \qquad (Equ^n\ 11)$$

so that equation (9) becomes

$$\frac{d^2u_2}{dr^2} + \phi\frac{u_2}{r} = 0 \qquad (Equ^n\ 12)$$

Now suppose

$$u_2 = \alpha_0 + \alpha_1.r + \alpha_2.r^2 + \alpha_3.r^3 + \cdots + \alpha_{n+1}.r^{n+1} + \alpha_{n+2}r^{n+2} + \cdots$$
$$+ \frac{\beta_1}{r} + \frac{\beta_2}{r^2} + \frac{\beta_3}{r^3} + \cdots + \frac{\beta_n}{r^n} + \frac{\beta_{n+1}}{r^{n+1}} + \cdots$$

Then

$$\phi.\frac{u_2}{r} = \phi.\alpha_1 + \phi\alpha_2.r + \phi.\alpha_3 r^2 + \cdots + \phi.\alpha_{n+1}.r^n + \cdots$$
$$+ \frac{\phi.\alpha_0}{r} + \frac{\phi\beta_1}{r^2} + \frac{\phi\beta_2}{r^3} + \cdots + \frac{\phi.\beta_{n+1}}{r^{n+2}} + \cdots \qquad (Series\ 1)$$

and

$$\frac{d^2u_2}{dr^2} = 2.1.\alpha_2 + 3.2.\alpha_3.r + \cdots + (n+2)(n+1).\alpha_{n+2}.r^n + \cdots$$
$$+ \frac{1.2.\beta_1}{r^3} + \frac{2.3.\beta_2}{r^4} + \cdots + \frac{n(n+1).\beta_n}{r^{n+2}} + \cdots \qquad (Series\ 2)$$

Comparing coefficients between series (1) and (2), we have

$$\alpha_0 = 0$$
$$\beta_1 = 0,\ \beta_2 = 0,\ \cdots,\ \beta_n = 0,\ \cdots$$
$$\alpha_2 = -\frac{\phi}{2.1}\alpha_1,\ \alpha_3 = -\frac{\phi}{3.2}\alpha_2 = +\frac{\phi^2}{3!2!}\alpha_1,$$
$$\alpha_4 = -\frac{\phi}{4.3}.\alpha_3 = -\frac{\phi^3}{4!3!}\alpha_1,\ \cdots,\ \alpha_n = (-1)^{n-1}.\frac{\phi^{n-1}}{n!(n-1)!}.\alpha_1,\ \cdots$$

Hence

$$u_2 = \alpha_1 r\left(1 - \frac{\phi}{2!1!}.r + \frac{\phi^2}{3!2!}.r^2 - \cdots + (-1)^{n-1}.\frac{\phi^{n-1}}{n!(n-1)!}.r^{n-1} + \cdots\right)$$

$$= \alpha_1 r\left\{1 - \frac{\left(2\sqrt{\phi.r}\right)^2}{2!\,1!} + \frac{\left(2\sqrt{\phi.r}\right)^4}{3!\,2!} - \cdots + (-1)^{n-1}.\frac{\left(2\sqrt{\phi.r}\right)^{2(n-1)}}{n!(n-1)!} + \cdots\right\}$$

Now if $J_1(x)$ is the Bessel function of the first order, then

$$J_1(x) = \frac{x}{2}\left\{1 - \frac{\left(\frac{x}{2}\right)^2}{2!\,1!} + \frac{\left(\frac{x}{2}\right)^4}{3!\,2!} - \cdots + (-1)^{n-1}\frac{\left(\frac{x}{2}\right)^{2(n-1)}}{n!(n-1)!} + \cdots\right\}$$

Hence

$$u_2 = \alpha_1 . r . \frac{2}{2\sqrt{\phi . r}} . J_1 \left(2\sqrt{\phi . r}\right) \qquad (Equ^n - 13)$$

in which α_1 is the integration constant. This is a solution of equation (12). Therefore the solution of equation (7) is

$$u = \beta_1 e^{-r\sqrt{\frac{K . \rho_{H\ell}}{\delta_1}}} + \frac{\alpha_1 r}{\sqrt{\frac{K . \rho_{H\ell} . r_0 . r}{\delta_1}}} . J_1 \left(2\sqrt{\frac{K . \rho_{H\ell} . r_0 . r}{\delta_1}}\right)$$

whence the solution of equation (6) is

$$\chi = \frac{A}{r} e^{-r\sqrt{\frac{K . \rho_{H\ell}}{\delta_1}}} + \frac{B}{\sqrt{\frac{K . \rho_{H\ell} . r_0 . r}{\delta_1}}} . J_1 \left(2\sqrt{\frac{K . \rho_{H\ell} . r_0 . r}{\delta_1}}\right) \qquad (Equ^n - 14)$$

(in which A and B are now the integration constants). Further, as this solution contains two integration constants, it is the general solution of equation (6).

Equation (14) thus represents the law of distribution of sodium vapour throughout the reaction chamber, if it is assumed that the experiment has been so regulated as to provide a suitable rate of entry of the carrier gas charged with sodium vapour into the chamber, and if it is permissible to assume that the distribution of the vapour of the halogen compound in the reaction chamber is affected only by the presence of the carrier gas, and not by the consumption of this vapour by the reaction.

Equation (14), it will be noticed, involves two terms and two integration constants A and B. It

thus involves three unknown parameters A, B and K. To determine these three quantities completely, three equations are required, which might be obtained by the adoption of three sets of limiting conditions. Two such sets have been suggested by von Hartel and Polanyi (12) (see pages 14 and 15), viz.,

$$x = p_{Na} \quad \text{at} \quad r = r_0$$

$$x = p_0 \quad \text{at} \quad r = R$$

A suitable third condition might be obtained by interposing between the sodium lamp and the reaction tube a medium, such as a plate of dark glass, which would raise the minimum partial pressure of sodium detectable when it was in use, to (say) p_1 , and again measuring the radius (say R_1) of the luminous sodium zone. A new limiting condition

$$x = p_1 \quad \text{at} \quad r = R_1$$

would then be obtained, and equation (14) used to find K.

Since, however, this procedure would increase considerably an experimental error which already (on account of the number of observations which have to be made in each experiment and of the rather strict condition which has to be aimed at in regard to the rate of flow of sodium vapour through the nozzle) is not small, and since the calculation of the results of an experiment would become exceedingly laborious, it seemed better to investigate first the possibility of simplifying equation (14).

For this purpose the two terms of equation (14) were considered separately. The first term

$$\frac{A}{r} \cdot e^{-r\sqrt{\frac{K \cdot \rho_{He}}{\delta_1}}}$$

is the value of x which satisfies the equation

$$\frac{d^2x}{dr^2} + \frac{2}{r} \cdot \frac{dx}{dr} - \frac{K \cdot \rho_{He}}{\delta_1} \cdot x = 0$$

which, as has been noted, was derived by von Hartel and Polanyi for the case of uniform distribution of the halogen compound vapour throughout the reaction chamber. It was also used in the calculation of K_α in the table on page 53. These values of K_α were found to be systematically inconstant, varying approximately as the reciprocal of R. A calculation shows, in fact, that $K_\alpha \times R$ or $K_\alpha \times (R - r_0)$ is not subject to any systematic error, but has values which are distributed at random about a mean value.

This suggests that the unsuitability of the equation

$$x = \frac{A}{r} \cdot e^{-r\sqrt{\frac{K \cdot \rho_{He}}{\delta_1}}} \qquad (Equ^n\ 15)$$

obtained by neglecting the second term in equation (14), for determining K, arises from the fact that in it r enters in the exponent to the first power, while K enters as $\sqrt{K}$.

Now in the second term

$$\frac{B}{\sqrt{\frac{K \cdot \rho_{He} \cdot r_0}{\delta_1} \cdot r}} \cdot J_1\left(2 \cdot \sqrt{\frac{K \cdot \rho_{He} \cdot r_0}{\delta_1} \cdot r}\right)$$

of equation (14), both K and r enter in the same way. Other things being equal, this would indicate that by neglecting the first term of equation (14) and using, to determine K, the equation

$$\chi = \frac{B}{\sqrt{\frac{K \cdot p_{He} \cdot r_0 \cdot \tau}{\delta_1}}} \cdot J_1\left(2\sqrt{\frac{K \cdot p_{He} \cdot r_0 \cdot \tau}{\delta_1}}\right) \qquad (Equ^n 16)$$

values for K would be found which would not be systematically dependent on R.

The use of this equation (16) for determining K will be discussed in connection with the experiments with chlorobenzene in the next section, and it may be said here, in anticipation, that by its use reasonably constant values for K are obtained.

Meanwhile, there remain one or two points to be discussed.

1. It is obvious from the derivation of equation (14) that the equation governing the distribution of sodium vapour in the reaction chamber would become even more cumbrous if account were taken of the variation of the diffusion coefficient of sodium vapour with the variation in the relative proportions of halogen compound vapour and carrier gas present at different points in the reaction chamber. In view of the dependence of the diffusion coefficient on the relative proportions of the gases in mixtures of hydrogen or nitrogen and pentane vapour found by von Hartel, Meer and Polanyi (13), it would appear that the simplest way of attaining to even approximately

accurate values for reaction velocity constants by this method, is to use directly as carrier gas some compound whose molecular constitution is fairly similar to that of the compounds investigated, and to assume that the diffusion coefficient of sodium vapour in the mixture in the reaction chamber will remain in these circumstances independent of the varying proportions of the mixture at different points in the chamber. For this reason the use of xylene vapour as carrier gas in the present experiments may be considered justified on theoretical grounds.

2. The exact significance of using equation (16) for determining K from the experimental observations is not easily seen. This equation is a solution of the differential equation

$$\frac{d^2x}{d\tau^2} + \frac{2}{\tau}\cdot\frac{dx}{d\tau} + \frac{K\cdot p_{He}\cdot r_0}{\delta_1}\cdot\frac{x}{\tau} = 0$$

which would be obtained from equation (1), page 63 , if the law of distribution of the halogen compound vapour were

$$y = -\frac{p_{He}\, r_0}{r}$$

a law which possesses no physical significance, since y, p_{Hl}, r_0 and r must naturally all be positive. From the fact, however, that equation (15) can be derived as the law governing the distribution of sodium vapour in the reaction chamber for the case of uniform distribution of the vapour of the halogen compound, we may suspect that the first term in equation (14) governs the distribution of sodium vapour for very large values

of r, when the partial pressure of the halogen compound vapour has become almost uniform, and that nearer the nozzle, where the distribution of the halogen compound vapour is considerably altered by the presence of the carrier gas, this term becomes of much less importance than the second term.

3. $J_1(x)$ is, of course, a function of x for any one value of which there exists in general a large number of values of x. There was found to be no dubiety, however, concerning the value of K as determined from equation (16), since all values except one were too large to be probable.

THE VELOCITY OF THE REACTION BETWEEN SODIUM VAPOUR AND CHLOROBENZENE.

The results of the preceding section may now be applied to the experiments described on pages 48 to 53, in which the velocity of the reaction between sodium vapour and chlorobenzene was investigated. The measurements made in those experiments are used for determining the velocity constant of the reaction in conjunction with the equation

$$x = \frac{B}{\sqrt{\frac{K.p_{He}.r_0}{\delta_1}.\tau}} \cdot J_1\left(2\sqrt{\frac{K.p_{He}.r_0}{\delta_1}.\tau}\right) \qquad (Equ^n\ 1)$$

where

x is the partial pressure of sodium vapour in a shell of the spherical zone of the vapour,

B is an integration constant,

K is the velocity constant of the reaction defined by

$$-\frac{dx}{dt} = K.x.p_{Hl}$$

p_{Hl} is the measured partial pressure of chlorobenzene in the reaction chamber,

r_0 is the radius of the nozzle,

δ_1 is the diffusion coefficient of sodium vapour in the gases in the reaction chamber,

r is the radius of the shell in which the partial pressure of sodium vapour is x,

and $J_1(X)$ represents the Bessel function of the

first order, of X.

In order to find the two unknown quantities B and K, we require two equations. These are obtained in the usual way by inserting the usual limiting conditions

$$x = p_{Na} \quad \text{at} \quad r = r_0$$

$$x = p_0 \quad \text{at} \quad r = R$$

where p_{Na} is the vapour pressure of sodium at the temperature of the sodium reservoir, and R is the measured radius of the luminous zone of sodium vapour.

These conditions give us the two equations

$$p_{Na} = \frac{B}{\sqrt{\frac{K \cdot p_{He} \cdot r_0}{\delta_1} \cdot r_0}} \cdot J_1\left(2\sqrt{\frac{K \cdot p_{He} \cdot r_0}{\delta_1} \cdot r_0}\right) \qquad (\text{Equ}^n\ 2)$$

and

$$p_0 = \frac{B}{\sqrt{\frac{K \cdot p_{He} \cdot r_0}{\delta_1} \cdot R}} \cdot J_1\left(2\sqrt{\frac{K \cdot p_{He} \cdot r_0}{\delta_1} \cdot R}\right) \qquad (\text{Equ}^n\ 3)$$

Eliminating B between equations (2) and (3), we obtain

$$\frac{p_{Na}}{p_0} = \frac{\sqrt{\frac{K \cdot p_{He} \cdot r_0}{\delta_1} \cdot R}}{\sqrt{\frac{K \cdot p_{He} \cdot r_0}{\delta_1} \cdot r_0}} \cdot \frac{J_1\left(2\sqrt{\frac{K \cdot p_{He} \cdot r_0}{\delta_1} \cdot r_0}\right)}{J_1\left(2\sqrt{\frac{K \cdot p_{He} \cdot r_0}{\delta_1} \cdot R}\right)}$$

or, expressed more conveniently

$$\frac{p_{Na}}{p_0}\sqrt{\frac{r_0}{R}} = \frac{J_1\left(2\sqrt{\frac{K \cdot p_{He} \cdot r_0}{\delta_1} \cdot r_0}\right)}{J_1\left(2\sqrt{\frac{K \cdot p_{He} \cdot r_0}{\delta_1} \cdot R}\right)} \qquad (\text{Equ}^n\ 4)$$

In this equation the only unknown quantity is K, but the equation cannot be rearranged to give K explicitly. The only method of finding K is to insert a series of trial values for it into the right-hand member of the equation until the value is found which makes the two members equal. Although this procedure sound tedious, it was found that with practice in the use of this equation the labour involved was not excessive.

The Bessel Function tables of Hayashi (24) were used, after interpolation to the third place of decimals in the argument, in these calculations.

The table of experimental results on the velocity of the reaction between sodium vapour given on page 53 is here reproduced, with the addition of a column of values for K determined from equation (4). In it also occurs a column K_c , which consists of the values of the velocity constant of the reaction determined from equation (4), but reduced to the units c.c. $mole^{-1}$ sec^{-1}, and a column E, containing the values of the activation energy of the reaction, determined from K_c and the Arrhenius-Trautz relation,

$$e^{-\frac{E}{RT}} = \frac{\text{Number of collisions at which reaction takes place}}{\text{Total number of collisions.}}$$

In finding the total number of collisions between molecules of sodium and chlorobenzene ~~from~~ the

expression (23)

$$Z = N_1 N_2 \sigma_{12}^2 \left\{ 8\pi RT\left(\frac{1}{m_1} + \frac{1}{m_2} \right) \right\}^{\frac{1}{2}}$$

was used

(in which

Z is the number of collisions between sodium and chlorobenzene molecules,

N_1, N_2 are the numbers of molecules of sodium and chlorobenzene present respectively in each cubic centimetre,

R is the gas constant,

T is the absolute temperature,

m_1, m_2 are respectively the weights of a sodium and a chlorobenzene molecule,

σ_{12} is the mean of the molecular diameters of sodium and chlorobenzene).

The value $5{\cdot}5 \times 10^{-8}$ was assigned to σ_{12}. A number of writers, e.g., (25), (26), (27), (28), (29), agree in giving the values $1{\cdot}7 \times 10^{-8}$ to $1{\cdot}9 \times 10^{-8}$ cm. as the radius of the sodium atom; while a calculation of the radius of the xylene molecule, assuming the viscosity coefficient of the vapour at 20°C to be 60 micropoises (see page 46) and the Sutherland constant to be 362 (an extrapolation from the work of Lowry and Nasini (21)) results in a value for the radius of $3{\cdot}8 \times 10^{-8}$ cm. at 275°C. It is not to be anticipated that the molecular diameters of xylene and of chlorobenzene or substituted chlorobenzenes will differ greatly, and the value $5{\cdot}5 \times 10^{-8}$ was used for σ_{12} throughout this work.

TABLE 2.

Results of Experiments on the Velocity and Activation Energy of the Reaction between Sodium Vapour and Chlorobenzene Vapour.

No.	T °K	T_{Na} °K	p_T mm.	R cm.	$f_c \times 10^8$ mols/sec	$f_{HCl} \times 10^8$ mols/sec	$p_{Na} \times 10^3$ mm	p_{HCl} mm.	δ_l	K_α	K_β	K	K_c	E cals/mole
2	547	536	1·12	2·0	143	470	2·98	0·86	198	336	1610	4180	1·42 × 10"	8730
3	553·5	540	1·14	1·5	166	490	3·53	0·85	198	901	3090	5650	1·95 × 10"	8490
5	548	539	1·09	1·9	194	500	3·39	0·785	204	492	2110	4970	1·70 × 10"	8550
6	547	536	1·09	2·1	193	490	2·98	0·78	203	329	1650	4500	1·53 × 10"	8650
7	546	533·5	1·39	0·9	63	450	2·67	1·13	159	1960	4670	5670	1·93 × 10"	8380
8	571	556·5	1·09	2·0	188	600	7·00	0·83	217	719	2470	4780	1·70 × 10"	8930
9	543	531	1·23	1·5	140	900	2·39	1·06	178	479	1920	4050	1·37 × 10"	8700
10	550	538	1·21	1·0	140	850	3·25	1·04	185	2080	5150	6470	2·22 × 10"	8290
11	557	545	1·20	1·25	151	810	4·37	1·01	190	1410	3880	5490	1·91 × 10"	8580
12	545	533	1·21	1·0	164	900	2·62	1·02	182	1800	4760	6470	2·20 × 10"	8220
13	555	543	1·39	1·1	274	580	4·01	0·94	163	1770	4480	5740	1·99 × 10"	8490
20	548	536	1·27	1·3	265	680	2·98	0·91	175	994	3190	5370	1·84 × 10"	8470
25	557	545	1·24	1·75	244	540	4·37	0·85	184	628	2280	4510	1·57 × 10"	8790
26	560	548	1·18	1·85	240	540	4·95	0·82	195	645	2340	4690	1·64 × 10"	8790

From the table, the following mean values are obtained:

$$K = 5180$$

$$K_c = 1{\cdot}78 \times 10^{11} \quad \text{c.c. mole}^{-1}\text{sec}^{-1}$$

$$E = 8600 \quad \text{cals/mole}$$

It would be arbitrary to assign any numerical value to the probable error in these experiments, depending as they do on a number of observations, several of which in turn depend on preliminary experiments. All the individual values for K and K_c in the table lie within twenty-five per cent of the above mean values. If the four experiments (2), (9), (10), (12), each of which gives values more than twenty per cent different from the mean values, are excluded, the average values from the remaining ten experiments are

$K = 5140$ $\quad K_c = 1{\cdot}78 \times 10^{11}$ c.c. $\text{mole}^{-1}\text{sec}^{-1}$

with which the individual values from the ten experiments are concordant within fourteen per cent.

It is to be noted in connection with the table that there is practically no variation of K or K_c with R. A very slight tendency for the smaller values of R to give larger values of K or K_c may be detected, but this does not militate against the significance of the values of K and K_c as do the variations with R of K_α and K_β in the case of these quantities. We may thus consider the use of equation (16) on page 70 to be justified by its success in practice.

On page 54 it was noted that the values for K_α and K_β obtained in the experiments under consideration were not only very inconstant but differed widely from the values obtained for the same reaction by von Hartel and Polanyi (12), who found K_α = 17,300, K_β = 17,270. The value of K was calculated from their figures and equation (4), page 74, and was found to be 8150. In view of the doubts expressed by those workers (loc. cit., page 124, footnote) concerning the partial pressure in the reaction chamber of the chlorobenzene vapour and of the uncertainty in their value for the diffusion coefficient of sodium vapour in the gases in the reaction chamber, it must be concluded that the difference between the value 8150 and the mean of the results of the present experiments is not greater than might have been expected.

THE VELOCITY Of The REACTION Between SODIUM VAPOUR And PARA-CHLORO-TOLUENE.

Para-chlorotoluene being somewhat less volatile than chlorobenzene, the flowmeter used was constructed separately from the reservoir for the liquid, and both flowmeter and reservoir were heated gently by electric windings, the currents through which were controllable by separate rheostats. After calibration of the flowmeter by the same method as was adopted for the case of chlorobenzene, reaction velocity experiments were commenced, the modus operandi being identical with that previously employed. The results obtained are given in the following table, in which the headings to the columns have the same significance as before (see pages 50-52 and 75), except that for "chlorobenzene", "para-chlorotoluene" is of course to be read in the case of the present table.

TABLE 3.

Results of Experiments on the Velocity and Activation Energy of the Reaction between Sodium Vapour and Para-Chlorotoluene Vapour.

No.	T °K	T_{Na} °K	p_T mm.	R cm.	$f_c \times 10^8$ mols/sec	$f_{Hl} \times 10^8$ mols/sec	$p_{Na} \times 10^3$ mm	p_{Hl} mm.	δ_1	K	K_c	E cals/mole
3	543	531	1·05	1·7	191	420	2·39	0·72	202	6180	2·09 × 10"	8240
4	551	539	1·05	1·7	194	420	3·39	0·72	213	6320	2·17 × 10"	8320
5	543	531	1·05	1·6	219	390	2·39	0·67	209	7060	2·39 × 10"	8090
6	548	536	1·05	1·6	210	390	2·98	0·68	211	7040	2·41 × 10"	8170
7	547	535	1·02	1·75	194	390	2·85	0·68	217	6620	2·26 × 10"	8220
8	554·5	542·5	1·01	1·7	206	390	3·93	0·66	224	7270	2·51 × 10"	8220
10	538·5	526·5	1·09	1·5	219	420	1·96	0·72	199	6650	2·23 × 10"	8100

From the table, the following mean values are obtained:

$K = 6730$

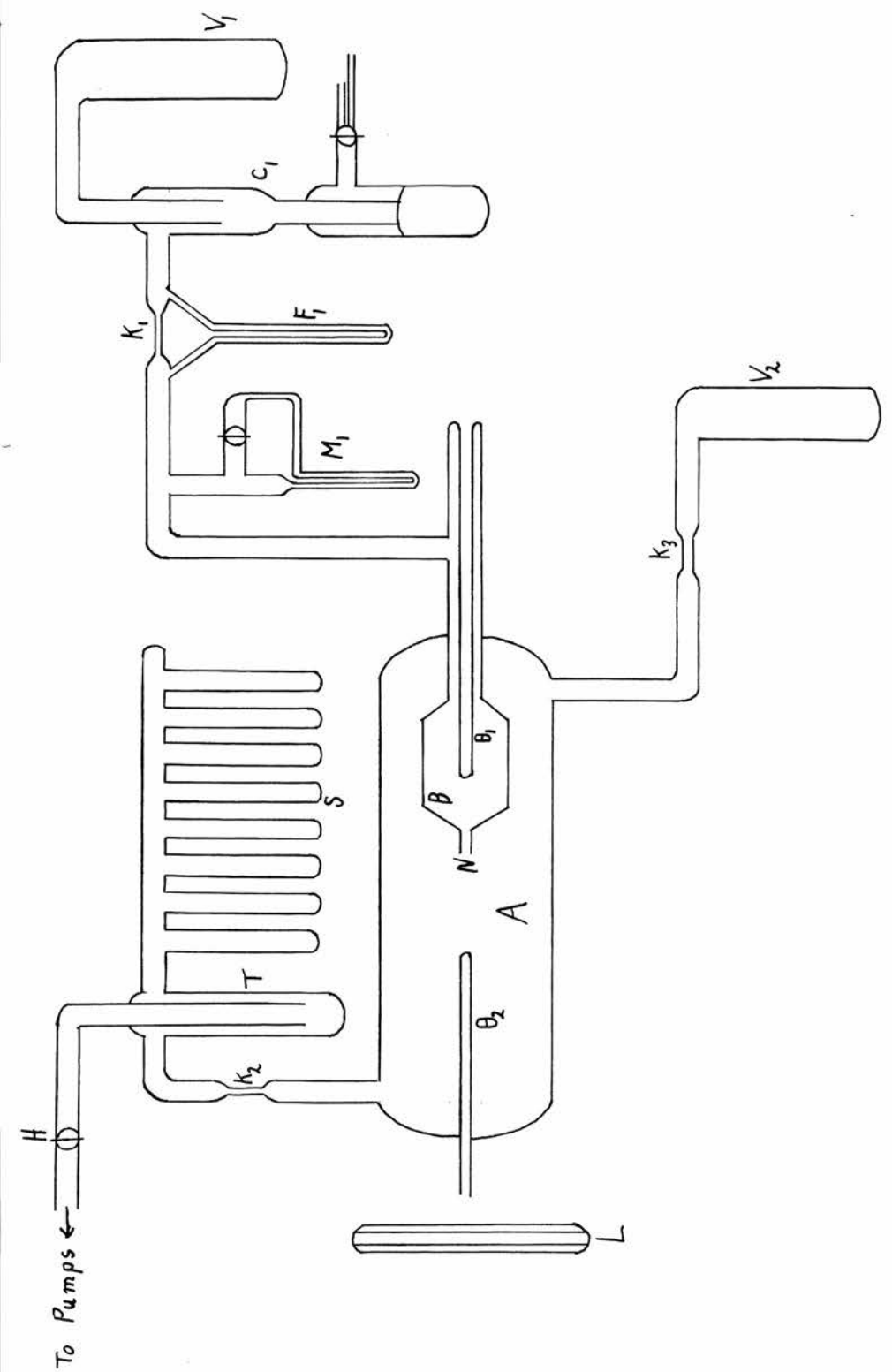
$K_c = 2{\cdot}29 \times 10^{11}$ c.c. mole^{-1} sec^{-1}

$E = 8200$ cals/mole

All the individual values for K and K_c in the table lie within ten per cent of these mean values.

THE VELOCITY Of The REACTION Of SODIUM VAPOUR With PARA-NITRO-CHLORO-BENZENE VAPOUR.

Para-nitro-chlorobenzene is considerably less volatile than either chlorobenzene or para-chlorotoluene, and preliminary experiments with the same arrangement of the apparatus as was used with the latter compound showed that to attain similar pressures of para-nitro-chlorobenzene in the reaction chamber, the flowmeter and the tube connecting the reaction chamber with the reservoir of the compound had to be heated so strongly that a considerable pressure of mercury vapour was attained in the reaction chamber. No simple modification of the apparatus was effective in avoiding this, and therefore the apparatus was altered according to the sketch on the following page.


To Pumps
H
K_2
T
S
B_2
A
N
B
B_1
L
K_3
V_2
M_1
K_1
F_1
C_1
V_1

Key to Letters.

A - The reaction chamber.

B - The sodium vessel.

N - The nozzle through which the sodium vapour was blown into the chamber.

θ_1, θ_2 - Tubes for thermocouples.

V_2 - The vessel for the halogen compound.

K_3 - A capillary of fairly wide bore - about 3 mm.

V_1 - The reservoir for xylene.

C_1 - A mercury cut-off.

F_1 - The flowmeter for xylene vapour, comprising a differential sulphuric acid manometer and the capillary K_1.

M_1 - A sulphuric acid manometer.

K_2 - A capillary.

T - A low temperature trap.

S - A set of tubes used in calibration experiments, as described below.

H - A stopcock.

The purpose of these modifications was to avoid the use of a flowmeter between the reaction chamber and the reservoir containing the halogen compound. Further, the manometer for determining the pressure in the reaction chamber was dispensed with to avoid condensation in it. The manometer M_1 was now used to determine this pressure, a small correction being applied for the pressure gradient across the nozzle N.

The rate of flow of xylene vapour into the reaction chamber could be measured by means of the flowmeter F_1 and the manometer M_1. The total rate of flow of the vapours out of the reaction chamber could be measured by the pressure difference between the ends of the capillary K_2. Now, one end of this capillary was near the trap T, and the pressure at this end may be regarded as zero. The pressure at the other end is the pressure in the reaction chamber, which was determined by the manometer M_1. Hence, after calibration, the total rate of flow out of the reaction chamber could be determined by reading the manometer M_1. From this and the known rate of flow into the chamber of xylene vapour, the rate of flow of the halogen compound could be determined by subtraction.

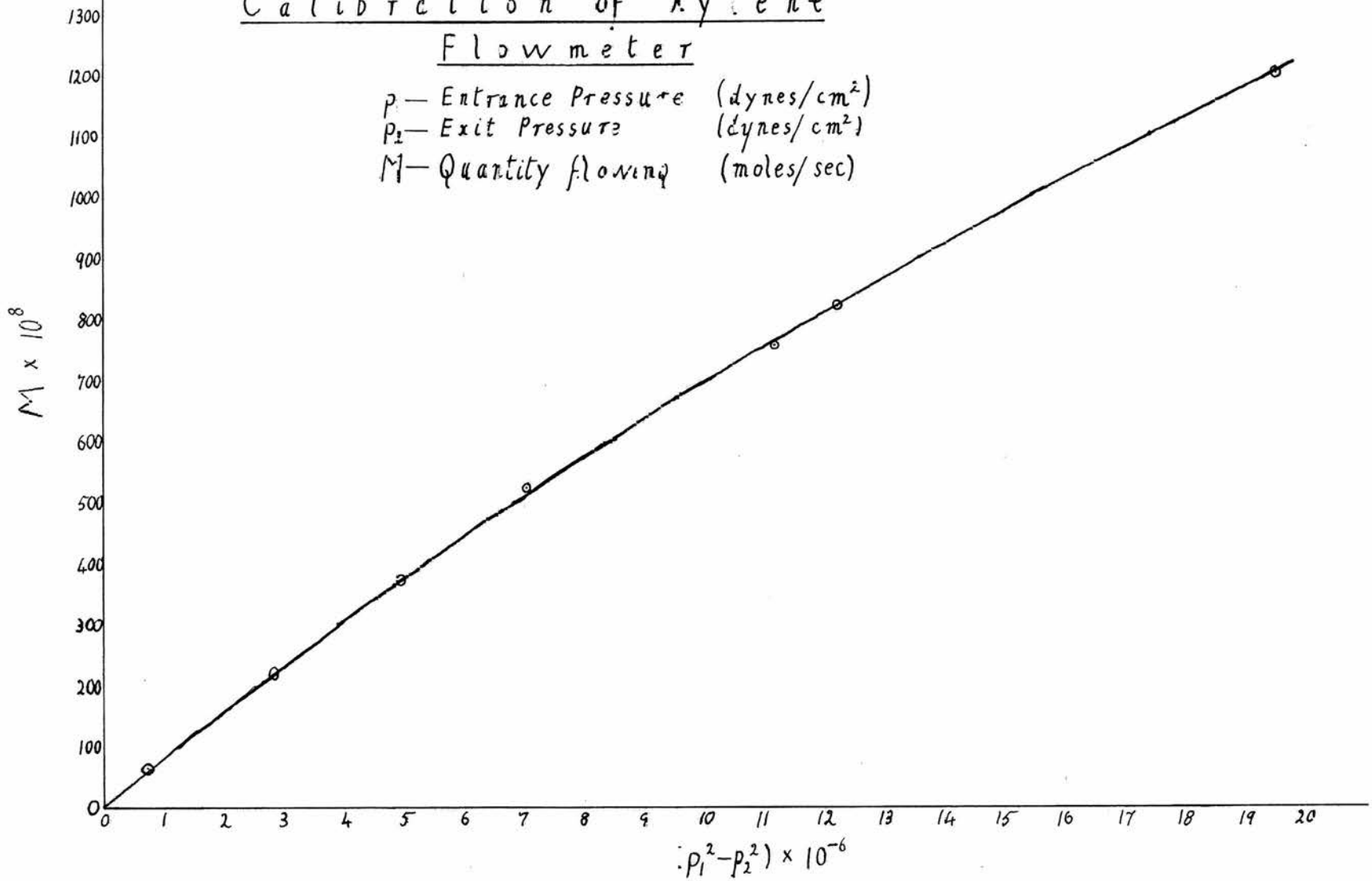
The capillary K_3 was inserted only to avoid any possible tendency of the halogen to bump over into the reaction chamber, by causing a slight pressure difference to develop across it.

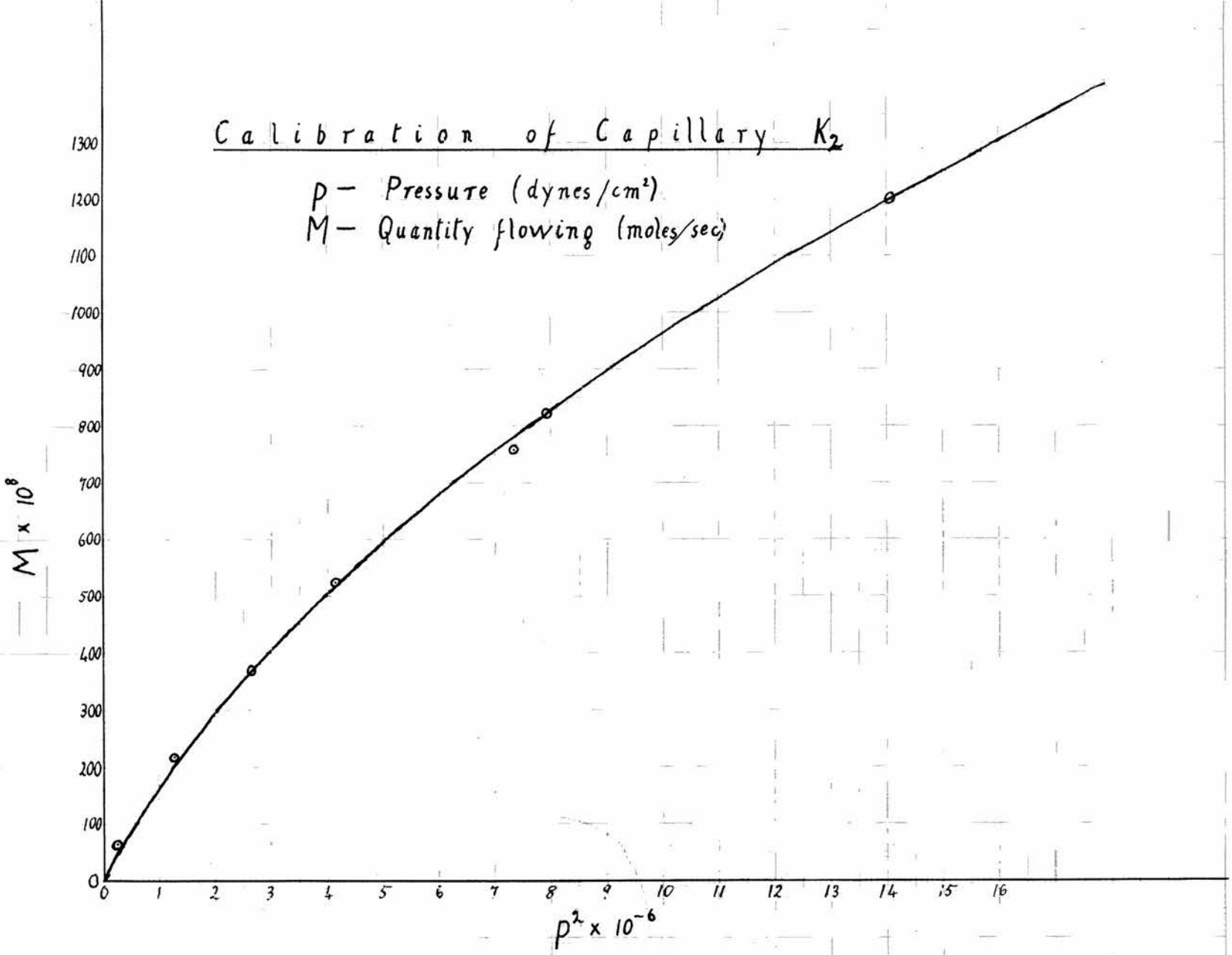
The calibration of the capillary K_2 was done with xylene vapour, and the opportunity was taken of simultaneously calibrating a rather more sensitive flowmeter F_1 for the xylene vapour. These calibrations were performed with the halogen compound vessel V_2 empty. The method of calibration was the same in principle as was used for the other flowmeters, namely, the passage of the vapour through the capillary, and the condensing of it in the trap T, for a known period of time, during which the readings of the flowmeter F_1 and the manometer M_1 were noted. The flow of xylene vapour was then stopped at C_1 , and the tap H was closed. One of the tubes S was then cooled by carbon dioxide snow and ether, while the trap T was allowed to warm up. In this way the xylene which had condensed was drawn over into the tube. When this process was complete (as indicated by the appearance of the trap T and by the return of the manometer M_1 to its zero), the tube was sealed off, scratched ready for cutting, and weighed. It was then opened at the scratch, the xylene removed by pouring off and then by pumping, and the tube again weighed. The whole experiment was repeated several times at different rates of flow of xylene vapour. The rate of flow was varied by varying the temperature of the xylene reservoir.

The rate of flow of xylene vapour per second was thus found, and was plotted against the difference of the squares of the pressures at the ends of the

Calibration of Xylene Flowmeter

p_1 — Entrance Pressure (dynes/cm^2)
p_2 — Exit Pressure (dynes/cm^2)
M — Quantity flowing (moles/sec)




Calibration of Capillary K_2
P — Pressure (dynes/cm²)
M — Quantity flowing (moles/sec)
M x 10⁸
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
P² x 10⁻⁶

capillary K_1 , as before. The reading of the manometer M_1 was then corrected, by means of the calibration curve of the former xylene flowmeter, for the pressure drop across the nozzle N, and the square of the pressure thus obtained was plotted against the rate of flow of xylene vapour, to serve as the calibration of the capillary K_2.

It should be noted that during these experiments the capillary K_2 was heated electrically to approximately the same temperature as that at which the reaction chamber was maintained during the reaction velocity experiments.

The two graphs of the calibrations of the xylene vapour flowmeter F, and of the capillary K_2 , are appended.

After the completion of these calibrations, para-nitro-chlorobenzene was distilled into the vessel V_2. (The first fraction which distilled was trapped in another tube and sealed off. Further, the distillation was stopped before all the compound had passed over. Thus only the middle fraction of the para-nitro-chlorobenzene was introduced into the apparatus.)

The apparatus was then used in the ordinary way to find the velocity constant of the reaction between sodium vapour and the vapour of the para-nitro-chlorobenzene. The capillaries K_2, K_3 were

electrically heated during the experiments to approximately the same temperature as the reaction chamber. The only difference in procedure was in the determination of the rate of flow of the para-nitro-chlorobenzene vapour into the reaction chamber, for which the method described above was used to give a first approximation to the value. It should be mentioned that the correction applied to the reading of the manometer M_1 was increased in these calculations (as compared with the correction used in the calibration experiments) by taking into account the increased viscosity coefficient of the xylene vapour at the temperature of the reaction chamber. A closer approximation to the actual rate of flow of the halogen compound was then obtained by correcting the viscosity coefficient of the effluent gases for the presence of the vapour of the halogen compound. In experiment number 1, for instance, the first approximation gave $f_{Hl} = 54 \times 10^{-8}$ mols per second, whence $p_{Hl} = 0{\cdot}21$ mm. of mercury. After correction for the increase in the value of the viscosity coefficient due to the presence of this partial pressure of para-nitro-chlorobenzene vapour, the values obtained were $f_{Hl} = 42 \times 10^{-8}$ mols per second, and $p_{Hl} = 0{\cdot}17$ mm.

The results obtained are given in the following table, in which the letters heading the columns have the same significance as before.

TABLE 4.

Results of Experiments on the Velocity and Activation Energy of the Reaction between Sodium Vapour and Para-Nitro-Chlorobenzene Vapour.

No.	T °K	T_{Na} °K	p_T mm.	R cm.	f_c $\times 10^8$ mols/sec	f_{Hl} $\times 10^8$ mols/sec	p_{Na} $\times 10^3$ mm	p_{Hl} mm.	δ_l	K	K_c	E cals/mole
1	547	535	0·92	1·75	186	42	2·85	0·17	241	29400	$10·02 \times 10^{11}$	6590
2	547	535	0·905	1·8	184	37	2·85	0·15	245	32900	$11·23 \times 10^{11}$	6470
5	545	533	0·90	1·7	170	47	2·62	0·20	245	26100	$8·88 \times 10^{11}$	6690
6	545	533	0·90	1·8	170	47	2·62	0·20	245	24700	$8·39 \times 10^{11}$	6750
7	545	533	0·90	1·4	164	52	2·62	0·22	245	28900	$9·80 \times 10^{11}$	6580
8	546	534	0·90	1·5	164	52	2·73	0·22	245	27000	$9·18 \times 10$	6670

From the table the following mean values are obtained:-

$K = 28200$

$K_c = 9{\cdot}58 \times 10^{n}$ c.c. $mole^{-1}$ sec^{-1}

$E = 6630$ cals per mole.

The individual values of K and K_c in the table do not differ by more than seventeen per cent from these mean values. It is to be noted, however, that the experimental error in these experiments may be expected to be higher than in those described earlier, because f_{Hl} , the rate of flow of the para-nitro-chlorobenzene vapour, is quite small, and is obtained as the difference of two quantities, each considerably greater than it. It is thus possible for quite small errors in each of these two quantities to cause a considerable error in f_{Hl}.

DISCUSSION Of The WORK.

Throughout this essay, the method devised by von Hartel and Polanyi (12) for determining the velocity constants of rapid reactions of sodium vapour has been discussed at some length, especially in the section "Mathematical Discussion of the Experiment" (page 57). It is, therefore, necessary to discuss here only a few points in connection with the experimental method.

Firstly, it may be said that the method, provided the calculation of the results was performed by the use of equation (16), page 70, proved to be remarkably free from the discrepancies and the variations with the conditions which are mentioned by von Hartel, Meer and Polanyi (13). Only a few of the experiments performed yielded results which lay outside fifteen per cent of the mean values. In the case of these few results, the source of the irregularity could sometimes be found - as, for instance, in the case of experiments 10 and 12 of table 2 , page 77, in which it was found that the high results were due to the condensation of sodium on the wall of the reaction chamber through which passed the light of the sodium lamp. The omission of experiments 14 to 19, and 21 to 24

from that table is accounted for by the fact that these experiments were performed at a much higher temperature (before the mathematical investigation had been carried out), in order to determine whether there was any error in the experimental procedure which could be brought to light by increasing the speed of the reaction. The results of these high temperature experiments are not included, as it was found later that they themselves were subject to a technical error in the procedure. Similarly, in the case of other experiments which are omitted, the sources of the discrepancies were often discovered to arise from errors in procedure.

It may, therefore, be claimed that the method as modified in the course of this work is subject to practically no inherent inconsistencies.

The question still remains, however, as to whether the values obtained for the reaction velocity constants may be regarded as absolute.

In this connection there must be considered the different assumptions made in the work described. They have been discussed when occasion arose, and need only be summarised here.

1. The assumption that the diffusion coefficient of sodium vapour in xylene vapour is not altered by the mixture of the latter vapour with that of a halogen derivative of benzene.

As has been mentioned, there is an *a priori* physical justification for regarding this assumption as valid, at any rate approximately. An accurate investigation of the diffusion coefficient of sodium vapour in the vapours of xylene and of, say, benzene would be required to determine just how true the assumption is in reality. On the other hand, the difficulty of using the results of such an investigation (mentioned on page 70) would seem to make its value of only theoretical interest, unless it proved possible to approximate to a better value of the reaction velocity constant by taking an average value for the diffusion coefficient in the gases in the reaction chamber. It may perhaps be anticipated that the values which would be obtained in this way for the reaction velocity constants would not differ very greatly from those found in the present work.

2. The assumption of the existence of a small zone near the nozzle, in which the partial pressures of the carrier gas and of the sodium vapour have not been diminished by the reaction or by diffusion.

This assumption would appear to be inherent in the experimental method, and it seems best to consider such a zone as having the radius of the interior of the nozzle.

3. The assumption, in the case of the modified experimental method used with para-nitro-chlorobenzene, that the viscosity coefficient of the mixture of gases effluent from the reaction chamber is dependent only on the proportions of the mixture, and on the molecular weights of the vapours comprising the mixture.

The validity of this assumption is of a higher order than the validity of assumption 1, concerning the diffusion coefficient of sodium vapour, in that some attempt has been made to correct for the variation of the viscosity coefficient with the proportions of the mixture. No further attempt at correction can be made without extensive investigation of the variation of the viscosity coefficients of mixtures of aromatic compounds with the proportions of such mixtures.

4. The assumption that the first term on the right-hand side of equation (14), page 67, may be neglected in comparison with the second term.

The validity of this assumption is shown, in part at least, by the regularity and consistency of the results obtained in this work. On the other hand, it must be mentioned that the absolute values for the reaction velocity constants can only be calculated if both terms are used. As to how near the values found

differ from the absolute values cannot easily be estimated, but in view of the wide variation of the velocity constants calculated by neglecting the second term, together with their regularity when calculated by neglecting the first term, it may be concluded that the difference between the real values and the values given in the tables on pages 77, 81 and 89 , is small, so far as this assumption is concerned.

The considerations above detailed would show that it is not to be expected that the values found for the velocity constants are ~~not~~ to be regarded as being the absolute values. On the other hand, the same considerations indicate that they will not be much different from the true values, and this is supported by the fact that the values found are of the order which would be expected from a priori considerations of the reactions investigated. Therefore, it may be concluded that the experimental method described in this essay will give values for the velocity constants of reactions, which are at any rate of the correct order, and are probably not widely different from the true values of the constants.

In this connection reference may be made to a new and important variation of the method, due to Frommer and Polanyi (30), which, while it is still in the stages of development, would seem to offer

possibilities for the determination of the absolute values of the velocity constants of reactions of the type investigated in this work.

With regard to the values found for the reaction velocity constants, it may be pointed out that the figures for chlorobenzene and for para-chlorotoluene are not very different, a result which is in conformity with general expectations from organic chemistry. Only one series of experiments has been found in the literature, in which reactions of chlorobenzene have been compared with similar reactions of substituted chlorobenzenes, namely, that of Krüger and Bednowa (31) who investigated the velocities of reactions of aromatic halogen compounds with sodium methylate. They found that the reactivities of the chlorine atoms in chlorobenzene and in para-chlorotoluene were as 1 to 0·6. In the present work it is found that para-chlorotoluene is slightly more reactive than chlorobenzene, but the difference is only small.

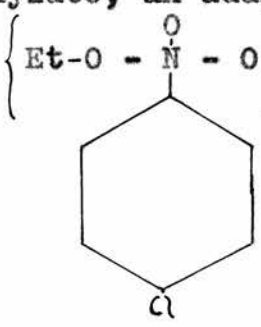
The result found for para-nitro-chlorobenzene is, however, of considerable interest. It is generally accepted by organic chemists that a nitro-group which is in the para-position to a chlorine atom in the benzene ring "activates" that atom greatly. Although only the above-mentioned workers have compared the reaction velocities of chlorobenzene with para-nitro-

chlorobenzene, yet it would in general be accepted that the latter compound would react at a speed of the order of a thousand times that of the former. Thus Davies and Wood (32) found that the activation effects of the nitro- and sulphonic acid groups in certain reactions were as 70,000 to 1. Krüger and Bednowa (loc. cit.) found the relative reactivities of the chlorine atoms in para-nitro-chlorobenzene and in chlorobenzene to be as 3600 to 1. The ratio of the figures obtained in the present work is 9·58 to 1·78 or 5·4 to 1.

Whether or not the values for reaction velocity constants found in the present work are absolute ~~or not~~, their departure from the true values should, at any rate, not vary widely from one compound to another. The very wide difference between the results of the present work and those of the organic chemists cannot, therefore, be explained on grounds of systematic errors in the experimental method. A possible cause of a large error in the reaction velocity constant found for para-nitro-chlorobenzene might be the presence in it of a considerably more volatile non-reactive impurity, which would contribute the majority of the value of p_{HI} found, while the para-nitro-chlorobenzene, present at a much lower partial pressure than that found, would in reality be the reactive substance present. Such a state of affairs would lead to gross error in the value of the reaction velocity constant which would

then appear much smaller than it really was. On the other hand, the fractionation of the para-nitro-chlorobenzene should certainly have made such an error most improbable.

On the other hand, the reality of the existence of a true activating effect of such magnitude, due to a nitro-group, has been questioned by some organic chemists, notably by Kenner (33). He has shown that the reactions of aromatic compounds containing such a nitro-group may be inhibited if the nitro-group is protected by the steric hindrance of a group close to it, not close to the atom or group to be displaced. Lindemann and Pabst (34) present a similar case. The view of these workers, which is discussed by Brewin and Turner (11), is that the unique position of the nitro-group in its activating effect, is due to its readiness to form addition compounds. The mechanism of the reaction as envisaged by Brewin and Turner, for instance, is that there is first formed, say in the reaction of para-nitro-chlorobenzene with sodium ethylate, an addition compound at the nitro-group, thus



and that subsequently there is an inter- or intra-molecular rearrangement with elimination of the

chlorine atom.

This view has, however, been questioned by Rheinlander (35) on the grounds that the effect of dilution on the velocities of reactions between sodium ethylate and certain bases, and halogeno-nitrobenzenes, is not compatible with the intermediate formation of addition compounds.

The question is still, from the point of view of organic chemists, undecided. In the reactions investigated in the present work, the mechanism is assumed to be that of a simple bimolecular reaction

$$ArCl + Na = NaCl + Ar$$

in the calculation of the results, and no inconsistencies are found to result. Further, Horn and Polanyi (36) have proved that the reaction between sodium vapour and bromobenzene leads to the production of free phenyl radicals, which is consistent with the assumed mechanism. The difference between the present results and those of the organic chemists would certainly appear to indicate that the reactions studied are quite different, and would suggest that some such mechanism as that suggested by Brewin and Turner (loc. cit.) is involved in the reactions in solution. It must further be noted that if the reaction between sodium vapour and para-nitro-chlorobenzene had a velocity of the order of 3000 times that of the reaction between sodium vapour and chlorobenzene, it would be a reaction with no energy of activation, which would make it

almost unique among reactions of compounds of such large molecules.

Perhaps it should be noted at this point that the possibility of a reaction between sodium atoms and the nitro-group of para-nitro-chlorobenzene has not yet been considered. Such a reaction is certainly possible, but in all probability is slow compared with the reaction with the chlorine atom. In connection with the present discussion, it may be added that if such a reaction did occur to an appreciable extent, the velocity constant of the reaction between the sodium atom and the chlorine atom of the compound would be less than that found, which would increase even more the difference between the results of the present experiments and those of organic chemistry.

S U M M A R Y.

A modification of the method of von Hartel and Polanyi has been used in an investigation of the reactions between sodium vapour and chlorobenzene, para-chlorotoluene and para-nitro-chlorobenzene, at about 275°C.

A new mathematical treatment of the experiment has been developed, which leads regularly to consistent values of the velocity constants of the reactions investigated.

The values found for the velocity constants and activation energies of the reactions investigated are:

1 $Na + C_6H_5Cl$ $K = 1{\cdot}78 \times 10^{11}$ c.c. mole^{-1} sec^{-1}
$E = 8600$ cals per mole

2 $Na + p\text{-}CH_3.C_6H_4.Cl$ $K = 2{\cdot}29 \times 10^{11}$ c.c. mole^{-1} sec^{-1}
$E = 8200$ cals per mole

3 $Na + p\text{-}(NO_2).C_6H_4.Cl$ $K = 9{\cdot}58 \times 10^{11}$ c.c. mole^{-1} sec^{-1}
$E = 6600$ cals per mole

A discussion of the experimental method and of the results obtained is presented.

In conclusion, I would express my gratitude to Dr E. B. Ludlam, under whose supervision the work described has been carried out, for his continued interest and encouragement. I would also acknowledge my indebtedness to the Carnegie Trustees for the grant of a Research Scholarship, during my tenure of which this work has been performed.

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